931. *The Polycondensation of Benzyl Chloride catalysed by Stannic Chloride.*[1]

By L. Valentine and R. W. Winter.

The kinetics of the polycondensation of benzyl chloride to form polybenzyl, catalysed by stannic chloride, have been studied. For each molecule of benzyl chloride consumed, one molecule of hydrogen chloride, the rate of evolution of which was measured, is evolved. Up to a catalyst concentration of 0·6M the rate is directly proportional to the concentration of catalyst; it then reaches a maximum at about 1·1M, and at higher concentrations becomes inversely proportional to the concentration of catalyst. Analysis of the conversion–time plots indicates that the reaction is of the first order in benzyl chloride, so that the empirical rate expression is

$$+d[HCl]/dt = -d[Ph \cdot CH_2Cl]/dt = k_1[Ph \cdot CH_2Cl][SnCl_4]/(1 + k_2[SnCl_4]^2)$$

where $k_2 \sim 1·0$. The activation energy is 7·9 kcal. per mole. The degree of polymerisation increases rapidly with extent of reaction at first, but becomes constant at extents of reaction $\geqslant 30\%$. At high conversions the degree of polymerisation is independent of temperature or concentration of catalyst. The reaction appears to be a polycondensation process proceeding by a chain reaction; probable reactive intermediates are discussed. Infrared and ultraviolet spectra of the polymers show that the structure is the same for polymers isolated at all stages of the reaction under any reaction conditions, and are consistent with the highly substituted polybenzyl structure proposed by Haas, Livingston, and Saunders.[2]

THE formation of a polymer from benzyl chloride, with the simultaneous evolution of hydrogen chloride, is an interesting example of a polycondensation process initiated by Friedel–Crafts catalysts. Such catalysts almost certainly owe their activity in vinyl polymerisations to the formation of ionic active intermediates. In view of the possibility that the polycondensation of benzyl chloride might have mechanistic affinities with ionic chain reactions, and the fact that no systematic study of the reaction had been made since modern views of polymerisation reactions were formulated, the kinetics of the reaction were investigated.

Benzyl derivatives of many different types, *e.g.*, fluoride,[3] chloride,[4] bromide,[5] and alcohol,[6] give rise to polymers that are generally called polybenzyls, although several structures have been suggested. A good summary of early work is given by Shriner and Berger [6] and also by Haas *et al.*[2] At the time this work was begun, it was thought that the polymers had a predominantly linear *para*-polybenzyl structure [6] (I), although some workers [3] preferred the pendant, or polystilbene, structure (II). Flory [7] had suggested

[1] A preliminary account of some of this work was presented at the International Symposium on Macromolecular Chemistry in Milan, 1954; Valentine and Winter, *Simposio Internazionale di Chimica Macromoleculare*, Supplement to *Ricerca sci.*, 1955, **25**, 95.

[2] Haas, Livingston, and Saunders, *J. Polymer Sci.*, 1955, **15**, 503.

[3] Ingold and Ingold, *J.*, 1928, 2249.

[4] Friedel and Crafts, *Bull. Soc. chim. France*, 1885, **43**, 53; Jacobson, *J. Amer. Chem. Soc.*, 1932, **54**, 1513.

[5] Boeseken, *Rec. Trav. chim.*, 1903, **22**, 312; 1904, **23**, 98.

[6] Shriner and Berger, *J. Org. Chem.*, 1941, **6**, 305.

[7] Flory, *J. Amer. Chem. Soc.*, 1952, **74**, 2718.

that the polymers might be branched polybenzyls, as reaction can occur at any of the three *ortho* and *para* positions. In the preliminary account of this work [1] it was suggested that spectroscopic data ruled out structure (I), and that accepted views of the structure might need modification. Since then, it has been suggested,[2] on the basis of spectroscopic, oxidation, and degradation data, that the polymers contain a nucleus of almost completely

$$\text{(I)} \quad \left[-\underset{}{\bigcirc} CH_2 - \right]_n \qquad\qquad \left[\begin{array}{c} -CH- \\ \bigcirc \end{array} \right]_n \text{(II)}$$

substituted benzene rings and have a periphery of pendant benzyl groups (III). In view of the uncertainty as to the structure of this interesting polymer, a re-examination of the spectroscopic evidence has been made.

Although many systems of the type benzyl derivative–Friedel–Crafts catalyst give rise to identical polymers (see p. 4776), benzyl chloride–stannic chloride was preferred because the reaction mixture is homogeneous throughout the reaction. whereas some catalysts (aluminium chloride, ferric chloride) yield some polymer insoluble in any solvent.

(III) *[structure of branched polybenzyl with Ph·CH₂, CH₂, H₂C, CH₂Ph, Ph substituents]* etc.
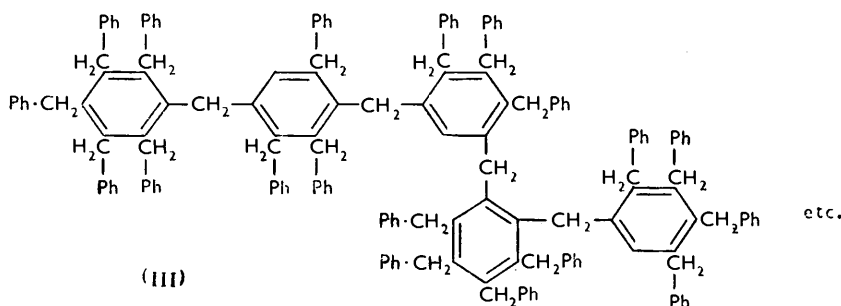
EXPERIMENTAL

Stannic chloride, benzyl chloride (redistilled), *n*-butyl alcohol, and dioxan were used as supplied (B.D.H.). Redistillation immediately before use of the benzyl chloride or stannic chloride did not affect the rate of the reaction. " AnalaR " sodium hydroxide was used. The benzene used in the viscosity determinations was also " AnalaR," redistilled from a trace of alcohol.

Method of following the Evolution of Hydrogen Chloride.—The reaction was followed by measuring the amount of hydrogen chloride evolved, which is directly proportional to the amount of benzyl chloride consumed. The polycondensations were carried out in a Pyrex tube fitted with a rubber bung carrying an air bubbler; these were dried at 105° immediately before use. Benzyl chloride (10 ml.) was pipetted into the reaction tube and allowed to reach the temperature of the bath (10 min.); the catalyst was then added from a microburette and the time noted. Air, dried by bubbling through concentrated sulphuric acid, was passed through to carry off the gas evolved, which was absorbed in a vessel holding 1 l. of distilled water, fitted with a device for withdrawing 15·0 ml. samples of the solution. Complete dissolution of the hydrogen chloride was achieved by the use of a sintered-glass bubbler and rapid stirring. A constant rate of flow of air of 3 ml. per minute was used.

Samples of this solution were withdrawn and titrated with 0·01N-sodium hydroxide, bromothymol-blue being used as indicator. Readings were taken initially every two minutes at 80°, and every five minutes at 0° and 25°; occasional readings were taken up to 3—6 hr., and finally a reading was taken after 24 hr.

All reactions were carried out in a thermostat bath controlled to ±0·05°.

Isolation of Polymer.—Two methods were used, depending upon whether the reaction went to completion (Method A) or not.

Method A. Dioxan (60 ml.) was added to the reaction mixture and the resulting solution

then added drop by drop to a large excess of ice-cold water, with constant stirring, the white precipitate being filtered off and dried *in vacuo* at room temperature. The crude product contained a fraction (1—3%), insoluble in organic solvents but soluble in hydrochloric acid to give the characteristic reactions of tin, which was filtered off before the polymer was reprecipitated from a solution in dioxan and dried as above.

Method B. Method A proved unsatisfactory if the polymer was isolated at low extents of reaction, when oily, discoloured products containing catalyst were obtained. Butyl alcohol (25 ml.), which dissolved the reactants but not the polymer, was added to stop the reaction, and the mixture stirred for 24 hr.; two further extractions with butyl alcohol were then made. The polymer was then filtered off, dissolved in dioxan, precipitated in water, and dried as above; no fraction insoluble in organic solvents was ever found.

General.—Viscosity measurements were made in an Ubbelohde suspended-level viscometer, modified to allow dilutions to be carried out in it. Solutions of polymer were made up in benzene and filtered through a No. 3 or 4 sintered-glass crucible; reproducibility was better if a No. 4 filter was used. The concentration of the final stock solution was determined by evaporation of the solvent.

Ultraviolet absorption spectra were determined on a Unicam spectrophotometer, chloroform as solvent and 1 cm. cells being used. Infrared absorption spectra were determined by Dr. J. H. Towler and Mr. B. H. Holland, of the University of Leeds, using a Grubb-Parsons single-beam instrument, or by Dr. E. Rothstein, also of the University of Leeds, using a Grubb-Parsons double-beam instrument, both with sodium chloride prisms. Over the range 1650—650 cm.$^{-1}$, 10% solutions in carbon disulphide were used, whilst over the range 2000—1650 cm.$^{-1}$, 50% solutions in carbon tetrachloride were used. Chlorine analyses were made commercially.

RESULTS

Kinetic Studies.—Despite the simplicity of the experimental techniques, the rates of evolution of hydrogen chloride were reproducible. The mean of at least two values, which usually agreed to within 5%, was used. Variation of the rate of passage of air through the reaction tube from 1 to 5 ml. per minute (30—160 bubbles) did not affect the results, nor did substitution of nitrogen for air. Under certain conditions, glass catalyses the polymerisation of aralkyl halides,[8] but we found no such effect.

Course of the Reaction.—Complete (*i.e.*, 100%) reaction is defined as the theoretical yield of hydrogen chloride in the reaction

$$nC_7H_7Cl \longrightarrow (C_7H_6)_{n-1} \cdot C_7H_7Cl + (n-1)HCl, \text{ where } n = 1000$$
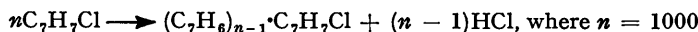
From this equation, 10 ml. of monomer (*d* 1·105), the amount always taken in this work, would give the yields of polymer and hydrogen chloride in Table 1 for various degrees of polymerisation.

TABLE 1

| Degree of polymerisation	2	4	6	10	17	52	1000
Amount of HCl (g.)	1·59	2·58	2·66	2·87	3·00	3·13	3·19
Amount of polymer (g.)	9·45	8·65	8·36	8·17	8·06	7·93	7·86

At 0°, a faint straw colour appears within 30 sec.; at higher temperatures the interval is shorter. No gas is evolved until the solution is orange. The colour intensifies throughout the reaction, and is deep red after about 12% reaction. The viscosity also increases and by 60—70% reaction the reaction mixture is a dark reddish-brown semi-solid mass expanded by bubbles of hydrogen chloride. Despite the great alterations in the nature of the reaction medium, the evolution of hydrogen chloride was smooth and continuous until reaction was complete.

Typical reaction curves at 0°, 25°, and 80°, for use of 0·165M-stannic chloride, are shown in Fig. 1. At all temperatures there is a short induction period (0—4% reaction) followed by an extensive period (4—40% reaction) over which the rate is practically constant, and finally by a continuous decrease in rate until the end. If a further 10 ml. of benzyl chloride were added to a reaction that had reached 56% conversion and was showing the normal rapid decrease in rate, another long period of constant rate (80% of the initial constant rate) was found. This shows that consumption of catalyst must be very small.

[8] Olivier and Wit, *Rec. Trav. chim.*, 1938, **57**, 1117.

A satisfactory mass balance between monomer and yield at 24 hours' reaction of polymer and hydrogen chloride was achieved (see Table 2). The sum of the weights of polymer plus hydrogen chloride is always 3—7% less than the weight of monomer introduced, probably

FIG. 1. *Course of reaction at various temperatures for* $[SnCl_4] = 0.165M.$
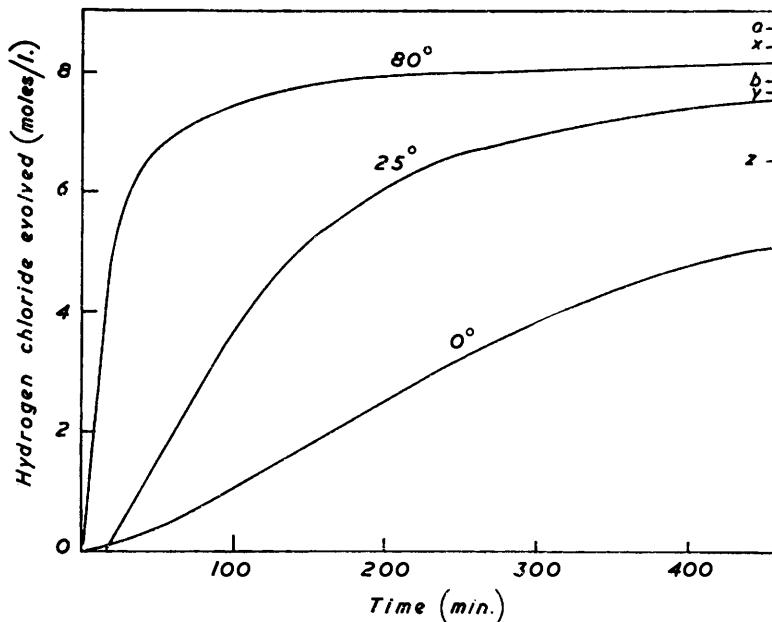
a, b; Theoretical yields of hydrogen chloride for 100% reaction to form polymers of degree of polymerisation ∞ and 10 respectively. x, y, z; Yields of hydrogen chloride after reaction for 24 hr. at 80°, 25°, and 0° respectively.

FIG. 2. *Residual monomer as a function of extent of reaction at* 25° *and* [SnCl₄] = 0.165M.

TABLE 2.

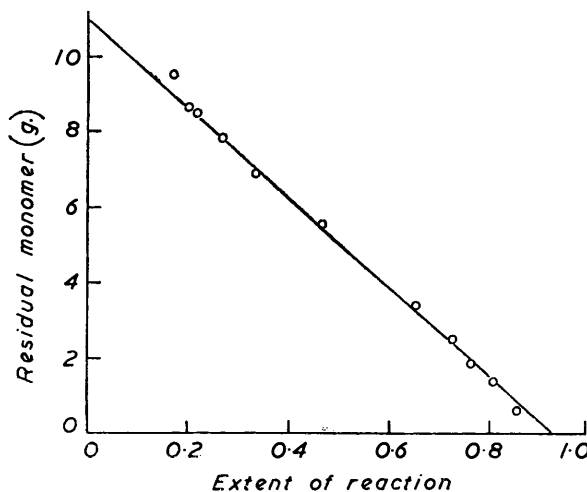| Temp.	[SnCl₄]	Polymer	Yield (g.) HCl	Total	Temp.	[SnCl₄]	Polymer	Yield (g.) HCl	Total
0°	0·165	7·80	2·70	10·50	70°	0·165	7·60	3·05	10·65
0	0·325	7·31	2·90	10·21	80	0·165	7·47	3·05	10·52
25	0·165	7·75	2·73	10·48	Theoretical for 100% reaction		7·86	3·19	11·05

owing to hydrogen chloride remaining in the reaction mixture, a loss of low molecular-weight polymers in the precipitations, and, at high temperatures, volatilisation of benzyl chloride.

The residual monomer at various extents of reaction was estimated by subtracting the sum of the weights of polymer and hydrogen chloride from the weight of monomer originally present. As shown in Fig. 2, the amount of monomer decreases linearly with extent of reaction; under these conditions ([SnCl$_4$] = 0·165M, 25°) the evolution of hydrogen chloride does not exceed about 91% reaction. However, there is no doubt of the linear correspondence between evolution of hydrogen chloride and consumption of monomer.
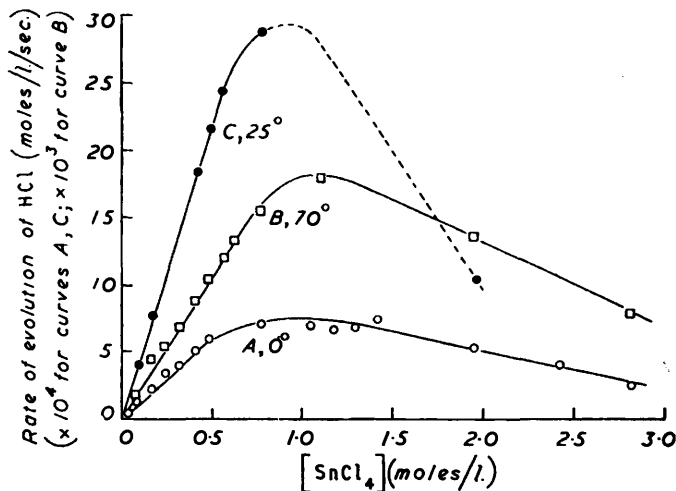

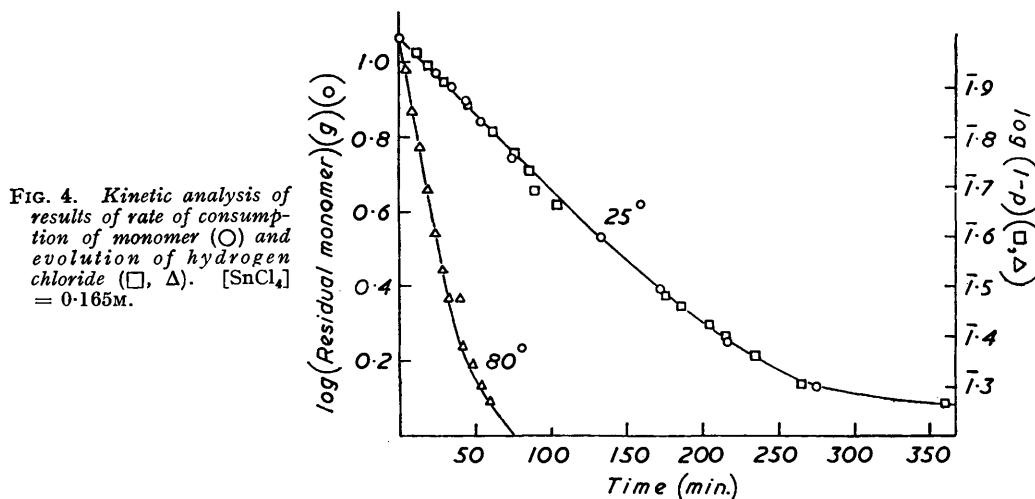Fig. 3. *Variation of rate with catalyst concentration.*

Fig. 4. *Kinetic analysis of results of rate of consumption of monomer* (O) *and evolution of hydrogen chloride* (□, △). [SnCl$_4$] = 0·165M.

Variation of Rate with Catalyst Concentration.—The effect on the rate of varying the concentration of catalyst is shown in Fig. 3. At all three temperatures the rate of evolution of hydrogen chloride is at first directly proportional to the catalyst concentration (0 to 0·6M), then reaches a maximum when the concentration of stannic chloride is about 1·0M, and thereafter declines. The rate at high concentrations of catalyst at 0° is inversely proportional to the catalyst concentration, and although there are fewer data at the higher temperatures, the general similarity of the curves makes it probable that a similar inverse relationship exists.

No account has been taken in Fig. 3 of the dilution of monomer by catalyst; for example, at the very highest concentration of catalyst used, the monomer concentration is only 5·82M, compared with 8·74M for pure benzyl chloride. Even if this decrease is allowed for (on the

assumption that the rate is of either first or second order in monomer concentration), the maximum is still found, although at a greater concentration of catalyst.

Order of Reaction with Respect to Monomer.—No experiments at varying concentration of monomer were made, but the kinetic order can be deduced from data on the extent of reaction as a function of time. The rate equation for a first-order reaction is $-kt = \ln M/M_0 = \ln (1 - p)$, where k is the rate constant, t the time, M_0, M the concentrations of reactant initially and at the time t, respectively, and p the fractional extent of formation of products. A plot of the logarithm of residual monomer against time (Fig. 4) is linear over a wide range (0—75% reaction), showing that the reaction is of the first order in monomer. The results have been corrected for the existence of an induction period of 26 min.

Analysis of the results of evolution of hydrogen chloride also indicates a first-order reaction, as shown in Fig. 4; $\log (1 - p)$ is a linear function of time over the range 0—60% reaction, if the induction periods are corrected for, in experiments at 25° and 80° ([SnCl$_4$] = 0·165M). Similar analyses result for other temperatures and concentrations of catalyst. The agreement between these two kinetic analyses is strikingly shown by the plots of the results for the experiment at 25°, both the evolution of hydrogen chloride and the consumption of benzyl
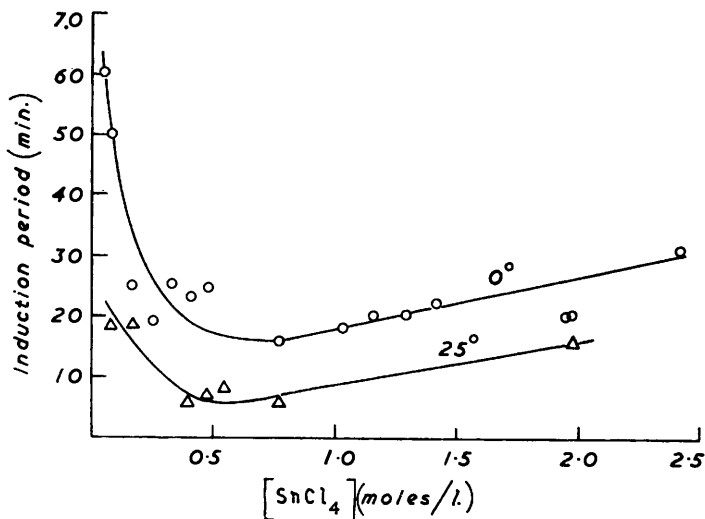

FIG. 5. *Variation of induction period with catalyst concentration.*

chloride fitting the same first-order plot. At very high degrees of conversion, a second-order plot fitted the results better.

The Induction Period.—Induction periods were estimated as the intercepts on the time axis of the linear portions of the plots of extent of reaction against time. As shown in Fig. 5, at a given temperature the induction period first decreases with increasing catalyst concentration, is afterwards virtually independent of the concentration, and finally at very high catalyst concentrations increases again. This is almost the inverse of the relation between rate and catalyst concentration. At 70° the induction period is so short (1—3 min.) that the experimental error is too large for any conclusions to be drawn.

Various experiments were made to ascertain if these induction periods were real. Spectrophotometric investigations of the development of colour revealed that the optical density initially increased almost linearly with time and then at an accelerating rate, until evolution of hydrogen chloride made further readings impossible. The induction periods in these experiments (in loosely stoppered test-tubes) were almost exactly the same as those found in the standard apparatus, suggesting that the induction periods are real. Benzyl chloride presaturated with dry hydrogen chloride gave no induction period, as shown in Fig. 6, but the desorption of monomer saturated with hydrogen chloride, but free from catalyst, had an induction period of about 10 min. It is difficult to reconcile these results. Most of the evidence, including that on the reaction between stannic chloride and polymer (p. 4776), supports the view that the induction periods are real, although the true kinetic induction periods may be shorter than the measured values.

Activation Energy.—Activation energies were calculated from the results represented in Fig. 3. As long as the rate is first-order in catalyst concentration, the activation energy (E) is 8·1 kcal. per mole, but there is a slight tendency for it to increase at high catalyst concentrations, as shown by the following figures (E in parentheses following stannic chloride molarity) 0—0·60 (8·1), 0·77 (8·2), 1·00 (8·2), 1·95 (8·6), 2·81 (9·0).

Effect of Water.—Water is often an essential cocatalyst in Friedel–Crafts polymerisations,[9] but
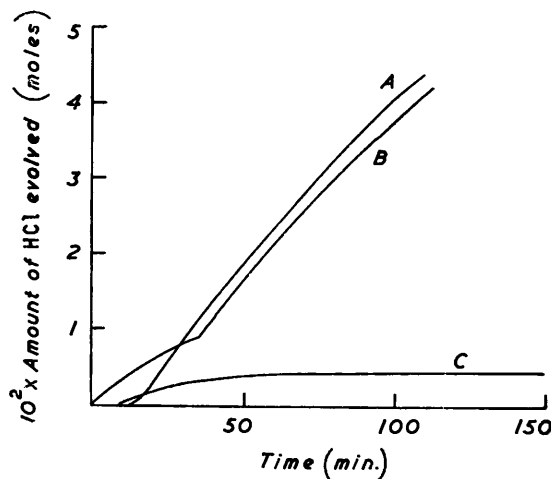

Fig. 6. *Effect of presaturation of benzyl chloride with hydrogen chloride on induction period at 25°.*
A ; [HCl] = 0, [SnCl$_4$] = 0·165M (control).
B ; [HCl] = saturated, [SnCl$_4$] = 0·165M (polymerisation).
C ; [HCl] = saturated, [SnCl$_4$] = 0 (loss or desorption).

Fig. 7. *Effect of water on rate of evolution of hydrogen chloride at 25°.* [SnCl$_4$] = 0·165M.
A, Ordinary benzyl chloride.
B, Benzyl chloride dried over anhydrous calcium sulphate.
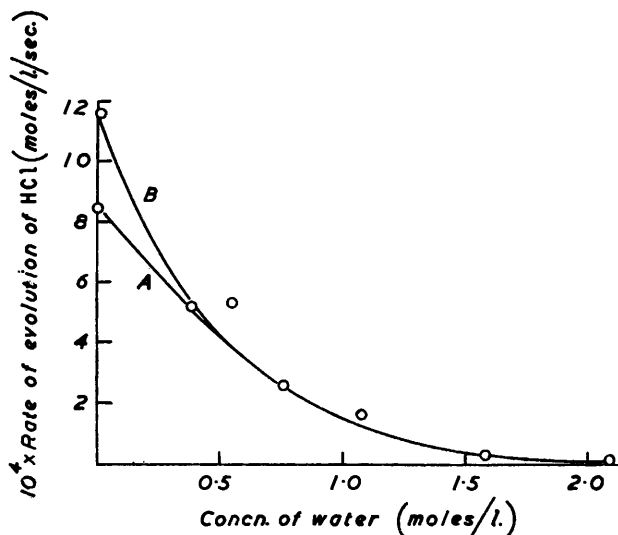
in the present reaction it appears to have merely a retarding effect, as shown in Fig. 7. Redistillation of the monomer immediately before use did not affect the rate, but redistillation followed by drying with anhydrous calcium sulphate for 16 hr. caused a 35% increase in rate. The general course of the reaction was exactly the same at all concentrations of water, even the slowest rates suffering a further decrease at long times of reaction, although the extent of reaction was less than 5%. Even when sufficient water had been added to form stannic chloride pentahydrate, the rate was still 27% of the value in the absence of water, although the solid

[9] Evans and Polanyi, *J.*, 1947, 252; Pepper, *Quart. Rev.*, 1954, **8**, 100.

pentahydrate had no catalytic effect whatever. The induction periods were unaffected by the presence of water.

Molecular-weight Measurements.—The limiting viscosity number was taken as a measure of the molecular weight, Bezzi's relation [10] between the cryoscopic molecular weight (M) and the viscosity of benzene solutions of polymer, prepared with aluminium chloride as catalyst, being used, viz., $(\eta - \eta_0)/\eta_0 c = 4\cdot01 \times 10^{-4}M$, where η, η_0 are the viscosities of solution and solvent, respectively, and c is the concentration in base moles per litre. In the units now approved,[11] $(\eta - \eta_0)/\eta_0 c = 4\cdot46 \times 10^{-3}M$, where c is now in g. per ml. Bezzi apparently measured the viscosity number $[(\eta - \eta_0)/\eta_0 c]$ in the range $c = 0\cdot01—0\cdot03$ g. per ml.; in this work, the data were extrapolated to zero concentration, but the limiting viscosity numbers $([\eta])$ so obtained do not differ from the viscosity numbers at $c = 0\cdot01—0\cdot03$ g. per ml. by more than 8%. As the viscosity ratio (η/η_0) was never greater than 1·8, even for 10% solutions, the experimental error in measuring the viscosity number is rather high.

In Table 3 the results of the viscosity measurements are summarised; all the polymers were obtained after 24 hours' reaction.
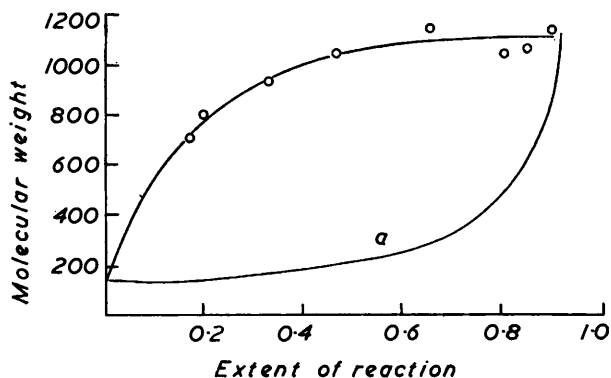

FIG. 8. *Variation of molecular weight with extent of polymerisation at 25°.* $[SnCl_4] = 0\cdot165M$.

a, Theoretical curve for a polycondensation mechanism.

The molecular weight is independent of the concentration of catalyst, and practically independent of the temperature, although there may be a slight rise in molecular weight as the temperature is increased, from about 1000 at 0° to 1150 at 70°. There is a definite increase in molecular weight with increasing extent of reaction, as illustrated by the results in Fig. 8.

TABLE 3. *Viscosity and molecular-weight determinations.*

$[SnCl_4]$ (moles/l.)	0°			25°			70°		
	$[\eta]$	M	k'	$[\eta]$	M	k'	$[\eta]$	M	k'
0·084	4·0	900	1·55	—	—	—	5·2	1190	0·86
0·165	—	—	—	4·6	1030	1·33	5·07	1140	0·95
0·246	—	—	—	5·34	1200	0·66	—	—	—
0·325	—	—	—	—	—	—	5·45	1220	0·84
0·478	4·2	940	1·65	4·88	1100	1·15	—	—	—
0·769	4·2	940	1·70	—	—	—	5·1	1140	0·95
1·10	—	—	—	4·94	1110	1·18	—	—	—
1·41	5·04	1130	1·08	—	—	—	5·25	1180	0·87
1·95	—	—	—	5·10	1150	1·10	—	—	—
2·42	4·6	1030	1·35	—	—	—	4·68	1050	1·08
Mean	4·4	990	1·47	5·0	1120	1·08	5·1	1160	0·92

At an extent of reaction of about 30—40%, however, the molecular weight becomes independent of the conversion.

As all the plots of viscosity number against concentration were linear, up to concentrations of 0·1 g. per ml., they were interpreted in terms of Huggins's equation $(\eta - \eta_0)/\eta_0 c = [\eta] + k'[\eta]^2 c$

[10] Bezzi, *Gazzetta*, 1936, **66**, 491.
[11] Report of Commission on Macromolecules of I.U.P.A.C., *J. Polymer Sci.*, 1952, **8**, 257.

From the values of k' listed in Table 3, there appears to be a fall in the value of k' as the temperature of the polycondensation is raised. There is a wide scatter in the values of k', however, because of its extreme sensitivity to changes in the value of $[\eta]$ for small values of $[\eta]$.

Reaction between Stannic Chloride and Polymer.—As mentioned above, an intense red colour develops during the reaction. Similar colours are often found in Friedel–Crafts reactions, *e.g.*, the aralkylation of benzene with benzyl chloride,[12] but in the present reaction the colour may be partly due to reaction between polymer and catalyst. Solutions of the pure polymer in benzene, chloroform, ethylene chlorohydrin, or mesityl oxide give intense red colours as soon as stannic chloride is added, which fade slowly. Aluminium chloride and sulphuric acid give similar effects, and both stannic chloride and aluminium chloride cause a similar colour reaction with solid polybenzyl. No simple benzene derivatives gives a red colour with stannic chloride, although several give a pale yellow colour. (Benzene, toluene, chlorobenzene, and polystyrene give no colour at all.) If stannic chloride is added to a solution of purified polybenzyl in benzyl chloride, an intense red colour develops instantaneously. The red colour persisting throughout the reaction may then be due to interaction between polymer and catalyst, and the slow development of colour in the induction periods is probably associated with the slow initial formation of polybenzyl.

Structure of the Polymer.—*Infrared spectra.* The infrared spectrum of a polybenzyl prepared at 25° with a concentration of catalyst of 0·165M has been reproduced.[1] Other workers[2] have obtained similar spectra, and from these and oxidative studies proposed the highly substituted structure (III). If the polymer is indeed highly substituted, it is important for the kinetic studies to determine the structure as a function of conversion. Accordingly, infrared spectra were determined of polymers isolated at the extents of reaction at 25° shown in parentheses from polymerisations with the following stannic chloride molarities : 0·165M (10, 25, 65, 75%), 0·40M (25, 40%), 1·41M (30, 75%). In addition, polymers isolated after virtually complete reaction with the following catalyst concentrations and temperatures were also examined : 0·33M (0°), 0·165M (25°, 80°). In every case, the spectra showed essentially the same features, *viz.*, two very strong bands at 697 and 727 cm.$^{-1}$, with an inflection at 743 cm.$^{-1}$, and no other bands in the region 700—820 cm.$^{-1}$ that are characteristic of other types of aromatic substitution. Small variations in the intensities, but never in the frequencies, of the bands occurred. The polymers prepared by the action of concentrated sulphuric acid on benzyl alcohol, or aluminium chloride on benzyl bromide, also have the same infrared spectrum and presumably the same structure.

The spectra were also determined in the region 1650—2000 cm.$^{-1}$, which usually affords one of the best methods for the identification of benzene-ring substitution. However, the results were inconclusive. All polymers showed three bands at 1970, 1930, and 1885 cm.$^{-1}$, of gradually diminishing intensity as the frequency is reduced, followed by a strong band at 1810 cm.$^{-1}$. This pattern differs from all the standard types listed by Young *et al.*,[13] but is not inconsistent with a structure composed of both highly substituted and monosubstituted rings.

Ultraviolet spectra. The ultraviolet spectra of two polymers prepared by using stannic chloride as catalyst have already been reproduced.[1] The main feature is a broad absorption band over the region 250—290 mμ, with three small peaks at 264, 266, and 270 mμ, the last being the main peak. Polymers prepared at 0°, 25°, and 80°, at various catalyst concentrations, all have the same spectrum, and the specific extinction coefficient, E [(optical density)/(path length in cm.)(concn. in g. per l.)], is 5·1—5·7. Polybenzyls prepared from benzyl alcohol or benzyl bromide have very similar spectra, although the extinction coefficients are somewhat higher.

DISCUSSION

Structure of the Polymer.—Our infrared results almost completely agree with those of Haas and his co-workers, in that there is no evidence of any type of benzene substitution other than monosubstitution in the characteristic region 700—850 cm.$^{-1}$. As polymers of virtually identical infrared spectra were obtained with a wide variety of initiators and benzyl monomers (in addition to those studied by us, the systems benzyl chloride–ferric oxide and benzyl fluoride–sulphuric acid also give polymers of identical spectra[2]), it seems

[12] Steele, *J.*, 1903, **83**, 1470.
[13] Young, duVall, and Wright, *Analyt. Chem.*, 1951, **23**, 709.

that all benzyl derivatives give polymers of essentially the same structure, no matter what catalyst is used. (This applies only to soluble polymers; some systems give insoluble polymers whose structures have not been determined.) The main difference between the present work and the previous infrared studies is that we find only two bands (at 697 and 727 cm.$^{-1}$, infl. at 743 cm.$^{-1}$), whereas Haas *et al.* report three bands, at 675, 695, and 725 cm.$^{-1}$. (The actual wave numbers were not quoted in the paper, but have been read from a spectrum kindly provided by Dr. H. C. Haas, whom we thank.) It is not clear why the band at 675 cm.$^{-1}$, which is attributed to a rocking vibration of the methylene group, should be absent in our polymers, but neither analyst found any trace of it. It is significant that the polymer has the same structure at all stages of the reaction, at least from 10% reaction onwards, as shown by the identity of the spectra in the regions 700—850 cm.$^{-1}$ and 1650—2000 cm.$^{-1}$.

The ultraviolet absorption spectra of all the polymers were also virtually indistinguishable. Although the general shape of the spectra is in accord with that expected for structure (III), the magnitude of the extinction coefficient is not. Monosubstituted benzenes generally have values of E of about 2, whilst the polybenzyls have values of 5 to 6. *para*-Substitution is usually the only type that gives rise to extinction coefficients of this magnitude for unconjugated hydrocarbon substituents, but in view of the strong evidence against *para*-substitution, the high absorption must be attributed to other, unknown, causes.

Unequivocal proof of the structure has not yet been attained, but as structure (III) provides the best explanation of the widest range of data, the discussion of the mechanism will be made on the assumption that the polymer has this structure, although the presence of small amounts of other structures cannot be ruled out. Chlorine contents of polymers prepared at various temperatures and catalyst concentrations ranged from 0·5 to 3·0% and showed no obvious dependence on either variable. The average value was about 1%, corresponding to the termination of only one polymer molecule in three by a chloride atom. The terminal chlorine atom may react with a side-chain benzyl group to form a dihydroanthracene derivative, *e.g.*,
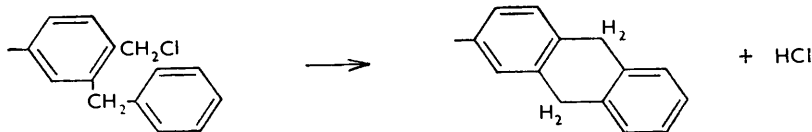
Such terminal groups would probably not be detected in either the infrared or the ultraviolet spectra. Cyclisation reactions of this type may also explain why in some reactions (see, *e.g.*, experiments at 70° and 80° in Table 2 and Fig. 1) the yield of hydrogen chloride is greater than that expected for polymers of a degree of polymerisation of about 12.

Mechanism of the Reaction.—The results given above show unequivocally that the mechanism is not of the normal polycondensation type, in which the degree of polymerisation increases as the reaction proceeds in accordance with the equation : Degree of polymerisation $= 1/(1 - p)$. As shown in Fig. 8, the molecular weight of the polymer becomes constant after 30% reaction. The behaviour expected in a stepwise polycondensation, shown in the same diagram, bears no resemblance to the experimental results. Attainment of a constant molecular weight early in the reaction is typical of chain polymerisations.

It has been suggested [14] that the molecular weights may be invalid because the degree of branching of the polymer may increase with extent of reaction. However, as the polymers have the same structure at all stages of the reaction and irrespective of the catalyst used, they would all be expected to satisfy the same relation between limiting viscosity number and molecular weight. The molecular weights are very low—too low, in fact, to permit the high degree of substitution and branching demanded by structure (III)—and Bezzi's

[14] Frank, *Simposio Internazionale di Chimica Macromoleculare*, supplement to *Ricerca sci.*, 1955, **25**, 109.

calibration may be in error.   This would not affect our conclusions, but merely the absolute values of the molecular weights.

Another criterion of a normal polycondensation is that the weight-fraction of monomer at any stage is given by $(1 - p)^2$, whereas for addition polymerisations the weight fraction is simply $(1 - p)$.   It is obvious from Fig. 2 that a stepwise polycondensation is ruled out.

The reaction is undoubtedly in many ways a typical Friedel–Crafts one, the main complications arising from the polymeric nature of the product.   When this work was begun, we thought the reaction probably involved benzyl cations, *e.g.*,

$$Ph \cdot CH_2Cl \ + \ SnCl_4 \ \rightleftharpoons \ Ph \cdot CH_2^+ \ + \ SnCl_5^-$$
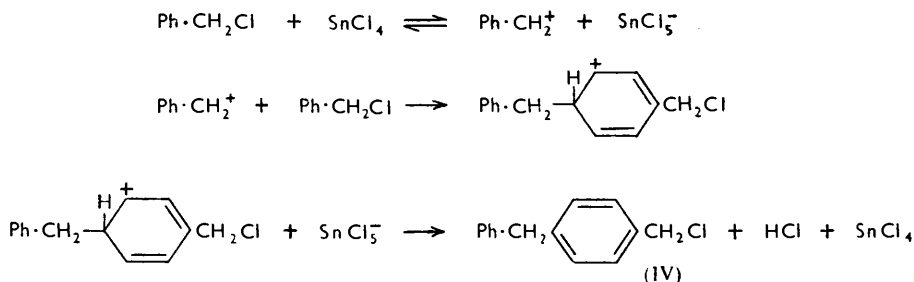
Polymers may readily be formed by reactions such as these on the dimer, trimer, etc. This view of the reaction was in harmony with the then accepted picture of Friedel–Crafts reactions.   Since then, however, H. C. Brown has suggested (see, *e.g.*, reference 15) that in the alkylation of aromatic compounds by primary halides, an un-ionised complex between the catalyst and the alkyl halide is involved, *e.g.*,
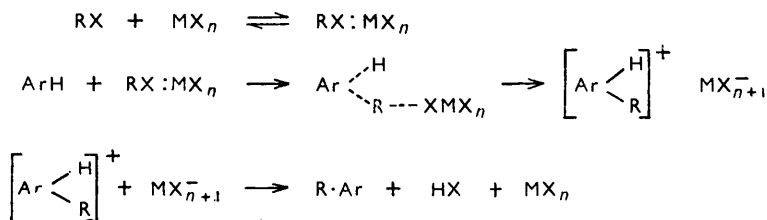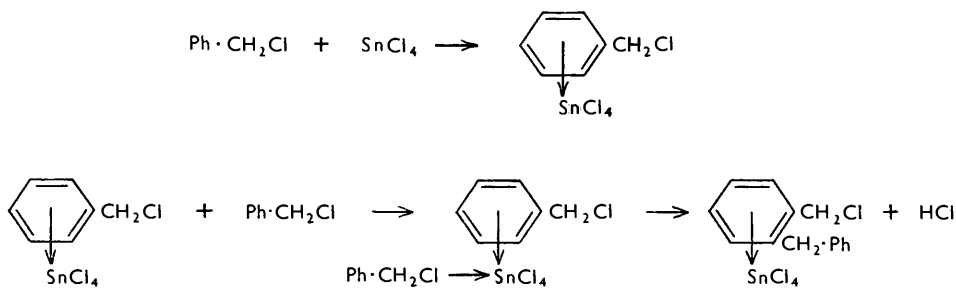
Brown and Wallace [16] have shown that the kinetics of the reaction of 3 : 4-dichloro-benzyl chloride with benzene are incompatible with the ionisation mechanism, but are in agreement with those expected from the displacement mechanism.   A similar reaction scheme can be applied to the autocondensation of benzyl chloride, if further benzylation of the primary product (IV) is allowed for.   [If structure (III) is accepted as correct, reactions involving the attack of the chloromethyl group of the polymer on monomer can be largely eliminated, as these could not lead to a highly substituted structure.]

However, it is difficult on either of these reaction schemes to explain the chain character of the mechanism.   Haas *et al.* have suggested that after the formation of the dimer, subsequent benzylation is much more rapid.   In terms of a chain reaction, the formation of the dimer may be regarded as the initiation step (slow), which is followed by the propagation steps of benzylation of the nuclear positions of the dimer (rapid).   The termination step may be non-existent in that the reaction may simply stop when all the nuclei of the dimer are substituted.   It may be significant that all the molecular weights correspond to that of the completely substituted dimer (1025).   The amorphous nature of the product, however, and its mechanical behaviour suggest that it is a mixture of polymers.

[15] Brown, Pearsall, Eddy, Wallace, Grayson, and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 1462.
[16] Brown and Wallace, *ibid.*, p. 6285.

Such a reaction might take place by way of either benzyl cations or complexes of monomer with stannic chloride, the latter possibly being π-complexes, *e.g.*,

$$Ph \cdot CH_2Cl + SnCl_4 \longrightarrow \text{[benzene ring with } CH_2Cl \text{, } SnCl_4 \text{]}$$

$$\text{[ring with } CH_2Cl, SnCl_4\text{]} + Ph \cdot CH_2Cl \longrightarrow \text{[ring with } CH_2Cl, Ph \cdot CH_2Cl \rightarrow SnCl_4\text{]} \longrightarrow \text{[ring with } CH_2Cl, CH_2 \cdot Ph, SnCl_4\text{]} + HCl$$

The complex between dimer and catalyst could then be further substituted, and so on. The chain would be terminated by elimination of the catalyst. Any mechanism must allow for regeneration of catalyst, which was demonstrated by the effect of adding fresh monomer to a partially reacted mixture (p. 4770). Each molecule of catalyst must be capable of converting about 100 monomer molecules into ten polymer molecules, since a catalyst concentration of 0·08M is sufficient to convert completely 8·74M-benzyl chloride into decamer.

However, the exact nature of the reaction will probably be elucidated only when ordinary Friedel–Crafts reactions are better understood.

At high concentrations of catalyst, additional complications arise. The empirical rate expression that fits the data at all temperatures and concentrations of catalyst is :

$$+d[HCl]/dt = k_1[SnCl_4][M]/(1 + k_2[SnCl_4]^2)$$

Since the maximum of the rate–catalyst concentration curve occurs at $[SnCl_4] \sim 1·0M$ at all temperatures, differentiation of the above expression and substitution of $[SnCl_4] = 1·0$ yields a value of k_2 of 1. The inhibiting effect of high concentrations of catalyst is perhaps analogous to other well-kmown changes in Friedel–Crafts reactions at molar concentrations of catalyst, *e.g.*, the change in orientation of substitution.[17] As the polymer prepared at high concentrations of catalyst still has the same structure and molecular weight, the mechanism is probably essentially the same. Stannic chloride may form two complexes, only one of which is active, the inactive form being favoured at high concentrations of catalyst.

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[17] Norris and Rubinstein, *ibid.*, 1939, **61**, 1163.