

339. *The Polymerisation of Styrene by Titanic Chloride.* *Part I. Kinetics.*

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The polymerisation of styrene by titanichloride in hexane, toluene, and various alkyl halides was investigated by an adiabatic technique. In the absence of deliberately added co-catalyst the reaction rate in hexane and in toluene could be made very small (zero in two experiments) by rigorous purification of the solvent. This slow reaction is considered to be due to adventitious co-catalyst, probably water. With trichloroacetic acid as co-catalyst the rate in toluene has an activation energy of -1.5 kcal./mole. In ethylene dichloride and dibromide the reaction rate is greatly accelerated by water. In the absence of water the rate in the former solvent is proportional to the catalyst concentration and the square of the monomer concentration. The activation energy is -8.5 kcal./mole.

THE polymerisation of styrene catalysed by metal halides has been studied quantitatively by several groups of workers in recent years (Gwyn Williams, *J.*, 1938, 246, 1046; 1940, 775; 1948, 1867; Pepper, *Nature*, 1946, 158, 789; *Trans. Faraday Soc.*, 1949, 45, 397; Medvedev and Gantmakher, *Zhur. Fiz. Khim.*, 1949, 23, 516; *Chem. Abs.*, 1949, 43, 7295; George, Mark, and Wechsler, *J. Amer. Chem. Soc.*, 1950, 72, 3891, 3896; Jordan and Mathieson, *Nature*, 1951, 167, 523; *J.*, 1952, 611, 621). These and related researches have been summarised and discussed in "Cationic Polymerisation and Related Complexes" (ed. P. H. Plesch, Heffer and Son, Ltd., Cambridge, 1953).

The present investigation was undertaken to discover whether the polymerisation of styrene by titanichloride, like that of *isobutene*, requires a co-catalyst, to find a suitable solvent for detailed investigations, and to obtain some more information on the chemistry and kinetics of this reaction.

EXPERIMENTAL

Apparatus.—The reaction vessel and its fittings are shown in Fig. 1. It was a flanged, double-walled vessel connected to a high-vacuum system so that the space between the walls could be evacuated at will. The flanged vessel-head carried a mercury-seal stirrer and four B. 14 sockets for admission of solvent, catalyst solution, and monomer and serving as inlets and outlets for dry nitrogen, the fourth socket carrying a thermometer. The flange and all joints and taps were lubricated with silicone grease.

The reaction vessel was connected to the solvent and catalyst reservoirs and burettes and to the dry nitrogen supply. All ducts opening to the atmosphere were protected from ingress of moisture by glass spirals embedded in carbon dioxide-ethanol.

Procedure.—The reaction vessel was swept out for about 2 hr. with dry nitrogen boiling off liquid nitrogen. After this the solvent was run in, either from a reservoir attached to the apparatus, *via* a burette, or by pipette (technique "A"). In later experiments it was distilled directly into the reaction vessel from an all-glass still, in an atmosphere of dry nitrogen, the quantity being gauged to the nearest 1 c.c. from graduations on the reaction vessel (technique "B"). When temperature equilibrium had been reached, the Dewar space of the reaction vessel being evacuated to a pressure of $<10^{-3}$ mm. Hg, the catalyst solution was run in from the reservoir *via* a burette. When an alkyl halide was used as solvent, the reaction was started by pipetting the monomer rapidly into the solvent-catalyst solution. When a hydrocarbon was used as solvent, the catalyst, co-catalyst, and monomer were usually added in this order, but, when it was desired to test whether an appreciable quantity of adventitious co-catalyst was present, the monomer was added after the catalyst, and after that, if necessary, the co-catalyst. Temperature readings on a mercury or pentane thermometer reading to 0.1° were taken at regular intervals until the reaction had subsided and the cooling rate was constant. For work at other than room temperatures the reaction vessel was surrounded by a suitable bath. In the later stages of the work it was found useful to add several portions of monomer to a given solution of catalyst, and to observe the polymerisation of each one in succession.

With ethylene dichloride as solvent this technique of repeated monomer addition made it possible to obtain a reasonable degree of reproducibility and to get results more rapidly. The disadvantage of this technique is that the molecular weight of the products of the individual reactions cannot be determined.

When the reactions were over, the reaction mixtures were poured into dilute sodium carbonate solution to hydrolyse the catalyst.

No attempt was made to calibrate the reaction vessels accurately, but from the temperature rises corresponding to 100% polymerisation of various quantities of styrene in 50 c.c. of ethylene dichloride it was found that a rate of 1°/min. was equivalent to an absolute rate of approx. 0.035 mole l.⁻¹ min.⁻¹ in this solvent. For 50 c.c. of toluene 1°/min. corresponded approx. to 0.032 mole l.⁻¹ min.⁻¹.

The adiabatic technique is justified because (a) there is no *a priori* reason why the rate of temperature rise should not be proportional to the rate of polymerisation provided the chain length is great enough to swamp the effect of the first one or two propagation steps for which the heat of reaction may be different from that of subsequent steps, (b) the total temperature rise during polymerisation is linearly related to the initial monomer concentration when

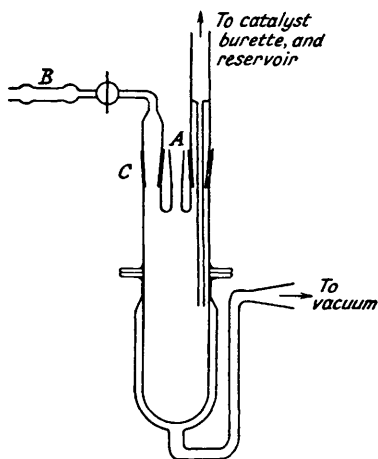


FIG. 1. *The reaction vessel.*

The internal dimensions of the reaction vessel are 5 × 12 cm.

A = Socket for mercury seal stirrer.

B = Calcium chloride tube.

The monomer is added through socket C. The sockets carrying the thermometer and the solvent inlet are not shown.

polymerisation is complete, and (c) the temperature changes involved and the activation energies are small.

Materials.—Styrene. Styrene (>99% pure, Koppers; 100 c.c.), stabilised with 4-*tert.*-butylcatechol, was shaken with 10% sodium hydroxide solution and twice with water, and left for 48 hr. on solid sodium hydroxide. It was distilled in a high vacuum from potassium hydroxide, and the middle fraction stored in a black bottle over potassium hydroxide powder. Even after several months it gave only a very faint turbidity (polystyrene) when poured into excess of ethanol; it had n_D^{25} 1.544.

Hexane. This was purified, and the titanous chloride solution in hexane prepared, as described previously (Plesch, *J.*, 1950, 543). The concentration of the latter was 0.3M.

Trichloroacetic acid. This was purified and its solution in hexane made up as previously described (*idem*, *ibid.*).

Toluene. Several specimens of toluene, purified in different ways, were used. Phosphoric oxide was not used for drying as it is appreciably soluble in toluene. Toluene I was purified by nitrous fumes, concentrated sulphuric acid, and dilute sodium hydroxide, distilled, pyrolysed by Szwarc's method (*J. Chem. Phys.*, 1948, 16, 128), and stored over calcium chloride. For toluene II, Catarex toluene (2½ l.) was refluxed for 1 hr. with aluminium chloride and then distilled through a 60-cm. Vigreux column; about three-quarters distilled over within 0.2° at a reflux ratio of 10 : 1. The distillate was washed with dilute sodium carbonate solution to free it from some aluminium chloride which came over with it. It was dried (CaCl₂) and distilled, and the fraction (almost 90%) distilling within 0.1° was collected and stored over calcium chloride. For toluene III, toluene II was refluxed for 1 hr. with 20 g. of sodium, then distilled and stored over fresh sodium chips. Toluene V was prepared from Catarex toluene in the same way as toluene I but, instead of being pyrolysed, it was refluxed with sodium, distilled, and

stored over calcium chloride. Toluene VI was prepared by treating toluene V successively with powdered calcium chloride, powdered soda lime, and phosphoric oxide, and distilling it and storing it over calcium chloride.

Ethylene dichloride. The commercial material (B.D.H.) was purified by shaking it successively with *n*-potassium hydroxide, water, and solid potassium carbonate. It was distilled from calcium chloride through a well-lagged 60-cm. Vigreux column with a reflux ratio of 5 : 1, and the fraction distilling over a range of 0.3° was collected. The yield was about 70%. If the ethylene dichloride was to be run into the reaction vessel it was stored over calcium chloride, since phosphoric oxide is appreciably soluble in it. If it was to be distilled into the reaction vessel it was stored over phosphoric oxide and later distilled from this.

Ethylene dibromide. The commercial product (Mersey Chemicals; ca. 450 c.c.) was treated four times with 98% sulphuric acid (25 c.c.), and washed with water, twice with dilute sodium carbonate solution, and again with water. It was dried (CaCl₂) and distilled off phosphoric oxide through a 60-cm. Vigreux column with a reflux ratio of 10 : 1; 350 c.c. distilled within a range of less than 0.1°; n_D^{25} was 1.538. It was stored over calcium chloride in the dark, and distilled off phosphoric oxide into the reaction vessel.

Measurement of Molecular Weight.—The intrinsic viscosities of the polystyrenes were determined viscometrically in toluene solution by the method previously described (Plesch, *loc. cit.*), and from these the mean molecular weights were calculated from the formula $[\eta] = KM^\alpha$, with Pepper's constants (*J. Polymer Sci.*, 1951, 7, 347), *viz.*, $K = 2.27 \times 10^{-4}$, $\alpha = 0.72$, the concentration being expressed in g. of polymer per 100 c.c. of solvent.

RESULTS

In a search for a suitable solvent, benzene and *cyclohexane* were discarded because their high f. p.s. restrict the temperature range over which the reaction can be investigated, and hexane because the insolubility of the polymer in it may complicate the kinetics; but some useful qualitative information was obtained with the last. Finally, toluene was chosen, and in spite of the extreme difficulty in purifying it, some qualitative results were obtained with it.

Hexane.—In Table 1 are given the initial rates of polymerisation of styrene by titanichloride in hexane solution without deliberately added co-catalyst, obtained by technique A. The rates are consistently very low. On addition of trichloroacetic acid the polymerisation was greatly accelerated and the ensuing reaction curves (time-temperature) were S-shaped.

TABLE 1. Rate of polymerisation of styrene in hexane and in toluene without deliberately added co-catalyst.

Expt. No.	Solvent	Temp.	Concn. of C ₆ H ₈ , mole/l.	Concn. of TiCl ₄ , m.mole/l.	Initial reaction rate, %/min.
371	C ₆ H ₁₄	22.5°	0.164	11.3	0
372	"	21.5	0.164	11.3	0.05
380	"	22	0.322	11.1	0.1
406	"	18.5	0.164	5.8	0.02
336	PhMe I	23	0.322	18.5	0.1
365	" I	-64	0.167	19.2	0
350	" II	25.5	0.322	18.5	11.6
368	" III	22°	0.322	18.5	0.7
370	" III	21.5	0.164	11.3	0.6
373	" III	22.5	0.164	11.0	0.4
381	" V	23	0.322	11.1	7
404	" VI	20.5	0.164	11.3	0.7
405	" VI	21.5	0.167	5.8	1.5

Toluene.—With technique A it was found that in toluene, however purified, it was not possible to obtain a non-reacting mixture of titanichloride and styrene, except at low temperatures. The residual reactivity ("blank" reaction) in the absence of deliberately added co-catalyst was very variable from batch to batch of toluene, and also varied slightly during the use of any one batch (Table 1). However, it was found that with toluene I, the slow "blank" reaction could be swamped effectively by using trichloroacetic acid as co-catalyst. The resulting reaction curves showed no acceleration, *i.e.*, the rate decreased monotonically from the initial maximum value. The reaction rate is proportional to a power of the concentration of trichloroacetic acid which is probably unity, but may be as high as 1.3 (Fig. 2). With toluenes II and V the "blank" reaction was very fast and the initial rates of polymerisation

actually diminished with increasing concentration of trichloroacetic acid; but the further treatment of both these samples described above gave toluenes III and V in which the "blank" reaction was much reduced.

In toluene I the activation energy of the initial polymerisation velocity with trichloroacetic acid as co-catalyst was -1.5 ± 0.3 kcal./mole (Fig. 3).

The molecular weights of the polystyrenes obtained in toluene solution with trichloroacetic acid as co-catalyst were not satisfactorily reproducible. They showed no trend with concentration of co-catalyst, and at a monomer concentration of 0.322 mole/l. and a catalyst concentration of 18 m.mole/l., they lay in the range of 500—800 at 25° and 1000—1200 at -62°.

In contrast to previous experience with *isobutene* (Plesch, *loc. cit.*) it was never found that the polymerisation ceased before all the monomer had been consumed. There is thus no evidence that the co-catalyst is consumed during the reaction. This is supported by the evidence from infra-red spectra presented in Part II (following paper).

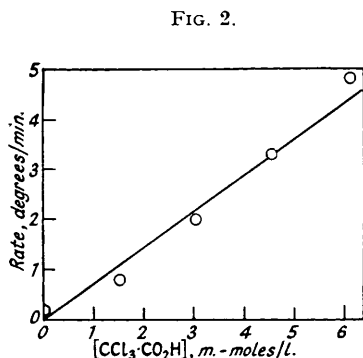


FIG. 2. The initial rate of polymerisation of styrene by titanous chloride in toluene as a function of the concentration of trichloroacetic acid.

Temperature 25°. Styrene concn. 0.322 mole/l., titanous chloride concn. 18.5 millimole/l.

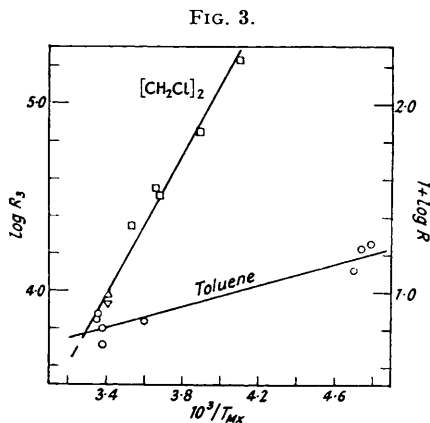


FIG. 3. Variation with temperature of the polymerisation rate of styrene by titanous chloride. T_{Mx} is the mean temperature of the interval over which the initial reaction rate was determined. The left-hand ordinate refers to experiments with $(CH_2Cl)_2$ as solvent (\square). Points ∇ and \triangle are derived from Figs. 5 and 6, respectively, the rest are individual experiments. R_3 is the third-order rate constant in degrees min^{-1} (mole/l.) $^{-3}$. The right-hand ordinate refers to experiments with toluene as solvent (\circ). In these the concentrations were: styrene 0.32 mole/l., $TiCl_4$ 19 m.-mole/l., $CCl_3 \cdot CO_2H$ 1 m.-mole/l. R is the observed initial rate of polymerisation in degrees/min.

These results make it highly probable that in hydrocarbon solution styrene is not polymerised by titanous chloride alone, but that a co-catalyst is necessary. This would be in agreement with Clark's results (Plesch, *op. cit.*, p. 99) obtained with the system styrene-boron fluoride-carbon tetrachloride.

Alkyl Halides as Solvents.—There is evidence to show that under the influence of catalytically active metal halides, alkyl halides can form positive ions (*e.g.*, Fairbrother, *J.*, 1941, 253), and Pepper (*Trans. Faraday Soc.*, 1949, 45, 397) has suggested that when styrene is polymerised in ethylene dichloride by stannous chloride the solvent acts as the co-catalyst. Ethylene dichloride, used by Pepper (*loc. cit.*), proved to be a very suitable solvent.

It was found impossible to obtain reproducible polymerisation rates as long as ethylene dichloride dried over calcium chloride was added by technique A; the reaction rate was excessively sensitive to traces of moisture, and when several portions of monomer were polymerised in the same solution, the rate of each successive polymerisation was less than that of the preceding one. When the solvent was distilled off phosphoric oxide directly into the reaction vessel (technique B), and the method of successive monomer additions used, the polymerisation rates were reasonably reproducible. It was found that up to 4 or 5 portions of 0.4 or 0.5 c.c. of styrene could be polymerised in the same batch of 40 or 50 c.c. of ethylene dichloride containing the titanous chloride, without any significant drift in the initial rates of the successive

polymerisations. This is illustrated in Fig. 4 and Table 2. The reaction mixtures were clear and pale yellow. The reaction goes virtually to completion. The yield was determined in several experiments by weighing the polymer contained in 5 c.c. of reaction mixture. In two typical experiments yields of 96% and 100.6% were found. The initial reaction rate was approximately proportional to the first power of the concentration of titanitic chloride (Fig. 5) and depended on the square of the initial monomer concentration (Fig. 6). Therefore $-dm/dt = R_3[\text{TiCl}_4][\text{Styrene}]^2$. The quantities R_3 and R_4 plotted in Figs. 5 and 6 are given by $R_3 = R_3[\text{TiCl}_4]$, with $[\text{Styrene}] = 1 \text{ mole/l.}$, and $R_4 = R_3[\text{Styrene}]^2$, with $[\text{TiCl}_4] = 1 \text{ mole/l.}$ The

TABLE 2. Polymerisation of styrene in ethylene dichloride by titanitic chloride.

Expt. No. ^a	T_{Mx} ^b	Concn. of TiCl_4 ^c m.mole/l.	Initial concn. of C_8H_8 , mole/l.	R_3 ^d degrees min. ⁻¹	R_3 ^e degrees min. ⁻¹ (mole/l.) ⁻³ $\times 10^{-3}$
412. I	21°	10.0	0.104	0.73	6.8
412. II	23	9.9	0.102	0.82	7.9
412. III	24	9.8	0.101	0.95	9.5
413. I	21	5.8	0.106	0.4	5.4
413. II	23	5.7	0.144	1.2	10.0
413. III	24.5	5.6	0.181	1.5	8.2
413. IV	22	5.6	0.0605	0.25	12.2

^a The Roman numerals indicate successive reactions carried out in the same batch of solvent-catalyst solution. ^b T_{Mx} is the mean temperature of the interval over which the initial reaction rate was determined. ^c This diminishes owing to the increase in volume of the reaction mixture due to the addition of successive portions of styrene. ^d Observed initial reaction rate, corrected for cooling. ^e Third-order rate constant, derived from the relation: Rate \propto [Catalyst][Monomer]².

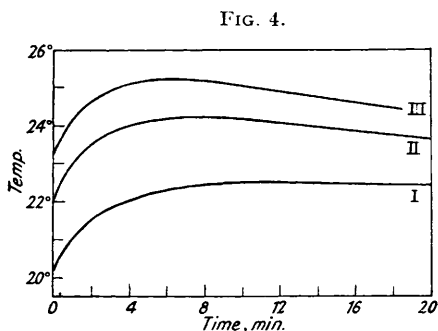
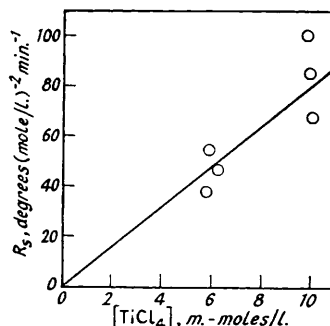


FIG. 4. Expt. 412. Typical time-temperature curves for the polymerisation of successive portions of styrene (I, II, and III) in the same solution of titanitic chloride in ethylene dichloride.

Concentrations as in Table 2.

In each run the styrene was added to the catalyst solution at time $t = 0$.

FIG. 5. Dependence of the second-order rate constant R_3 of the polymerisation of styrene in ethylene dichloride, on the concentration of titanitic chloride, at 20°.



temperature dependence of the third-order rate constant R_3 in degrees (mole/l.)⁻³ min.⁻¹ is shown in Fig. 3. The overall activation energy is $-8.5 \pm 1.5 \text{ kcal./mole}$. The third-order rate constant at 25° is of the order of $10^3 \text{ mole}^{-2} \text{ l.}^2 \text{ min.}^{-1}$, which leads to an A factor of about 10^{-3} in the same units.

The effect of water on the reaction rate was studied qualitatively by starting a reaction in the usual way by adding a portion of monomer to the catalyst-solvent mixture, and then, after following the reaction for some minutes, adding 2 c.c. of ethylene dichloride saturated with water (water content approximately 0.2 millimole). The reaction mixture became slightly turbid and its yellow colour deepened markedly. The actual reaction rate increased immediately by a factor of about 40 (reaction 417, IA, Table 3). After this reaction had subsided, further portions of styrene were added. The initial rates of successive reactions diminished steadily, but the rate of the last reaction was still about 4 times greater than that to be expected in the absence of deliberately added water. This experiment is illustrated in Fig. 7 and Table 3. It indicates that in the presence of water either this or the catalyst or both are consumed during the polymerisation. Reaction 417, IA is the very fast reaction which ensued upon the addition

of moist ethylene dichloride to the reaction mixture when about one half of the first portion of styrene had reacted.

TABLE 3. *Effect of water on the rate of polymerisation of styrene in ethylene dichloride by titanitic chloride.*

Expt. No.	Concn. of TiCl_4 , m.-mole/l. ^a	Concn. of C_8H_8 , mole/l. ^a	R , ^b degrees min. ⁻¹	R_c , ^c degrees min. ⁻¹ (mole/l.) ⁻²
417. I	5.85	0.0771	0.25	42
417. I \	5.7	~0.04 ^d	~2	1250
417. II	5.65	0.0742	3.3	600
417. III	5.55	0.0729	1.9	360
417. IV	5.50	0.0722	1.2	230
417. V	5.45	0.0715	0.9	180

^a The concentrations vary because of the increase in volume of the reaction mixture as successive additions are made to it. The volume of styrene added each time was 0.4 c.c. ^b Initial rate corrected for cooling. ^c R corrected to a monomer concn. of 1 mole/l. according to the relation $R \propto [\text{Monomer}]^2$, but not corrected for variation in catalyst concentration. ^d Somewhat less than half the monomer had reacted when the 2 c.c. of $\text{C}_2\text{H}_4\text{Cl}_2$ saturated with water was added (see Fig. 7).

These results show that in the absence of adventitious or deliberately added water, styrene is polymerised by titanitic chloride in ethylene dichloride, and this reaction is ascribed to the co-catalytic activity of the solvent.

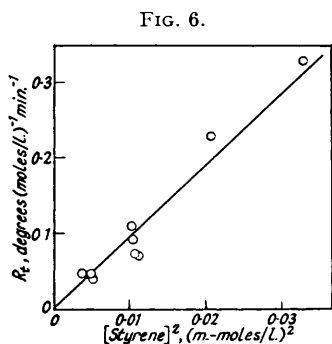


FIG. 6. *Dependence of the first-order rate constant R_1 of the polymerisation of styrene by titanitic chloride in ethylene dichloride, on the square of the monomer concentration, at 20°.*

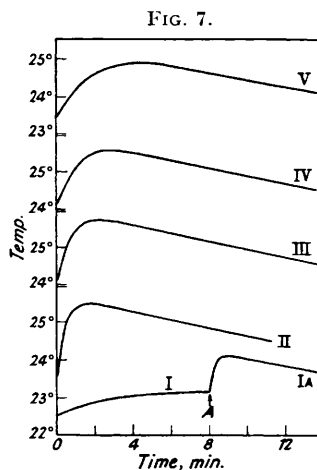


FIG. 7. *Expt. 417. The effect of water on the rate of polymerisation of styrene by titanitic chloride in ethylene dichloride.*

At *A*, 2 c.c. of ethylene dichloride saturated with water were added to the reaction mixture. Concentrations as in Table 3. Roman numerals indicate successive additions of styrene.

Ethylene dibromide was tried as solvent under the same conditions as with ethylene dichloride. Preliminary experiments showed that in this solvent the polymerisation of styrene by titanitic chloride is at least 100 times slower than in ethylene dichloride. The polymerisation is accelerated enormously by small traces of water. Since the reaction rate was so small and not very reproducible, the question whether this solvent can act as co-catalyst remains open.