1041. *The Polymerisation of Styrene by Titanium Tetrachloride. Part IV.*[1] *Kinetics of Polymerisation in Methylene Dichloride*

By W. R. Longworth, C. J. Panton, and P. H. Plesch

The kinetics of the polymerisation of styrene by titanium tetrachloride in methylene dichloride were investigated at −25°, −60°, and −90° by an adiabatic high-vacuum technique. The results obtained by two operators at an interval of two years with different equipment agree closely. The polymerisations are stationary of the first kind, of second order in monomer, and of a complicated order with respect to titanium tetrachloride and water. Two initiation reactions, one dependent on water, the other not, co-exist, and the former, which has a large normal temperature coefficient, becomes undetectable at −90°. The only chain-breaking reactions detected are a unimolecular termination and transfer reactions involving impurites and water. There is no evidence that the chain-carriers are ions. The whole behaviour pattern is completely different from that of isobutene polymerising under the same conditions.

There is only one kinetic study of the polymerisation of styrene by titanium tetrachloride, by a rather primitive technique.[1] The object of the present work was to obtain information on this reaction by improved methods so that a direct comparison could be made with the results of parallel studies on the polymerisation of isobutene in the same solvent and with the same catalyst.[2]

The present results have been obtained by two operators (W. R. L. and C. J. P.) working with two very similar sets of apparatus, two different temperature recorders, and many batches of materials. Most of the results obtained by the two workers agree closely, where they overlap. The results and their interpretation differ in some respects from those presented earlier which are now to be regarded as superseded.[3,4]

Experimental

Materials.—The purification of titanium tetrachloride [5] and of methylene dichloride,[5] and the preparation of the catalyst phials,[6] have been described. The methylene dichloride was stored over calcium hydride under its own vapour pressure in a reservoir attached to the reaction apparatus; it was frequently refluxed and degassed for at least 2 weeks before use.

Styrene used in the CP series of experiments was freed from inhibitor by shaking it successively with 30% aqueous potassium hydroxide and water and was then fractionally distilled from barium oxide under reduced pressure.

The middle fraction (b. p. 57·5°/30 mm.) was placed over calcium hydride and degassed until no hydrogen bubbles were evolved when the drying agent was agitated. It was then distilled under vacuum, large head and tail fractions being rejected, and the middle fraction was stored at 0° in the dark over barium oxide that had been pumped and flamed for several hours. The styrene was distilled through a metal tap [7] into phials attached to a manifold which had previously been extensively pumped and flamed. The amount of monomer in the phials was determined by the mid-point method.[8] The styrene used in experiments ST1—25 was freed from inhibitor, dried for 24 hr. over solid sodium hydroxide, and fractionated under reduced pressure; the middle fraction was stored at −4° in the dark over solid potassium

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[1] Part III, P. H. Plesch, *J.*, 1953, 1662.

[2] R. H. Biddulph, P. H. Plesch, and P. P. Rutherford, *J.*, 1965, 275.

[3] W. R. Longworth and P. H. Plesch, International Symposium on Macromolecules, Wiesbaden, 1959, Paper III A, 11.

[4] "Chemistry of Cationic Polymerisation," ed. P. H. Plesch, Pergamon Press, London, 1963, ch. 6.

[5] W. R. Longworth, P. H. Plesch, and M. Rigbi, *J.*, 1958, 451.

[6] R. H. Biddulph and P. H. Plesch, *Chem. and Ind.*, 1956, 567.

[7] R. H. Biddulph and P. H. Plesch, *Chem. and Ind.*, 1956, 569. (Available from Scientific Instrument and Model Co., Ross-on-Wye, Herefordshire.)

[8] P. P. Rutherford, *Chem. and Ind.*, 1962, 1614.

hydroxide. It was then transferred to the vacuum system, degassed, and fractionated by bulb-to-bulb distillation and stored in the dark over freshly crushed potassium hydroxide. The styrene used in experiments ST26 *et seq.* was dried in a manner similar to that adopted by Colclough and Dainton.[9] In a vessel attached to the high-vacuum apparatus it was degassed and refluxed at 20° for 8 hr. over barium oxide, then fractionated through a 60-cm. vacuum-jacketed column packed with glass helices. The column was then connected by the breaking of a magnetic break seal to an assembly consisting of a flask containing calcium hydride and one containing barium oxide; this part of the apparatus had been pumped and flamed for 5 days. The middle fraction of the styrene was distilled on to the calcium hydride and after 48 hr. it was distilled on to the barium oxide, and the first flask was sealed off. From the barium oxide reservoir, kept at 0°, portions of styrene were distilled through magnetic break-seals into a dosing burette from which the required quantities of styrene were distilled through a metal tap into the reaction vessel.

Phials containing measured amounts of water were prepared gasometrically on a high-vacuum manifold treated with trimethylchlorosilane.[2]

Apparatus.—The high-vacuum adiabatic reaction vessel and its ancillary reservoirs have been described.[10] The polymerisations were followed by means of the temperature rise which was registered for the ST series on the home-made recorder described [10] and for the CP series on a Sefram GR2VAD high-speed pen recorder.

Operation.—Two alternative methods of working were used by C. J. P., depending upon how the water content of the system was to be determined. (i) If a constant, but unknown, amount of water was to be used in a series of experiments, then water phials were omitted and the apparatus was pumped for a constant period before each polymerisation. (ii) When known amounts of added water were required, a water phial was included in the apparatus. In these experiments the concentration of residual water was reduced to a very low value by pumping the system for 5 hr. before carrying out the polymerisation.

When the reaction vessel had been pumped for the required time, 100 ml. of solvent were run in. The monomer phial [in procedure (i)], or the monomer and water phials [in procedure (ii)] were then broken and their contents stirred into the solvent at room temperature. The reaction vessel was then cooled to the working temperature with liquid nitrogen. When the rate of cooling was small and constant (not more than 0·2 deg. min.$^{-1}$) the catalyst phial was broken. The temperature rise due to the ensuing polymerisation was traced as a curve on the recorder, and the reaction was deemed to have ceased when the rate of after-cooling of the reaction mixture was approximately the same as the rate of pre-cooling. Air was admitted to the reaction vessel and any effect on the reaction trace was noted. After, or in the absence of, any effect, the reaction vessel was dismantled and its contents were poured into 600 ml. of slightly ammoniacal ethanol in order to precipitate the polymer and neutralise the catalyst; the dry polymer was weighed.

W. R. L.'s procedure was essentially the same, except for the minor point that the styrene was distilled into the reaction vessel, and the major one that the phial containing the water was not broken at room temperature, but at the low operating temperature, usually together with the catalyst phial. This difference turned out to be critical.

The concentration ranges used were: [Styrene] = 0·086 to 0·30, [$TiCl_4$] = (0·53 to 4·12) × 10^{-3}, [H_2O] = 0 to 6·42 × 10^{-4}M.

Measurements and Calculations.—The initial rate of reaction was measured by adding together the slope of the tangent to the reaction curve at the point of initiation and the slope of the tangent to the cooling curve.

In order to measure the internal order and internal rate constant of the polymerisations by Wilkinson's method,[11] the temperature rise during the reaction was required; it was measured by Dickinson's method.[12] The concentrations of reactants were computed for ambient temperature and corrected for the contraction of the solvent at the working temperature. The degree of polymerisation (D.P.) of the polystyrenes was obtained from the intrinsic viscosity of benzene solutions at 25° by Pepper's equation.[13]

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[9] R. O. Colclough and F. S. Dainton, *Trans. Faraday Soc.*, 1958, **54**, 886.

[10] R. H. Biddulph and P. H. Plesch, *Chem. and Ind.*, 1959, 1482.

[11] R. W. Wilkinson, *Chem. and Ind.*, 1961, 1395.

[12] H. C. Dickinson, *Bull. Bur. Stand. Washington*, 1914, **11**, 188.

[13] D. C. Pepper, *Sci. Proc. Royal Dublin Soc.*, 1951, **25**, 239.

RESULTS

All concentrations are given in moles/l. The experiments of W. R. L. are denoted by ST in the Tables and shown as open circles in the figures; those of C. J. P. are denoted by CP and shown as filled circles.

In all Tables and Figures [H_2O] means the concentration of *added* water.

The reacting solutions were pale yellow and clear, and the polymer remained in solution at all temperatures. The isolated polymer was white and friable.

W. R. L. could not obtain incomplete reactions at −30° even by the most careful procedure, whereas C. J. P. found that at −25° very long pumping and flushing of the apparatus with the vapour of trimethylchlorosilane would cause the reactions to stop at about 70% conversion with the old apparatus and at about 50% conversion with the new apparatus. This suggests that in W. R. L.'s work residual water or other co-catalytic impurity was more abundant than in C. J. P.'s.

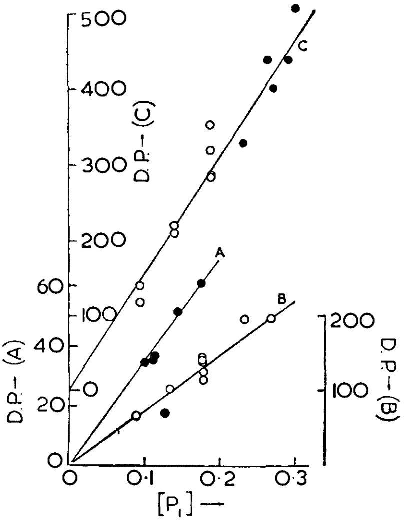

FIGURE 1. The dependence of the D.P. on the monomer concentration

○ W. R. L., ● C. J. P. A −25°, B −63°, C −91°. [H_2O] = 0, *i.e.*, residual after 5 hours' pumping

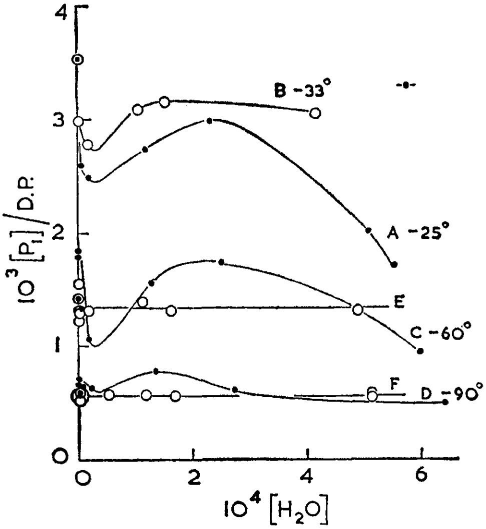

FIGURE 2. Mayo plot showing the dependence of the D.P. on the concentration of added water

○ W. R. L., ● C. J. P. -●- C. J. P. using W. R. L.'s technique at −25°. A −25°, B −33°, C −60°, D −90°.

The half-lives of the reactions ranged from 12 to 120 sec. At all temperatures and concentrations the rate of reaction decreased monotonically from the start; there was no sign of an accelerating phase in any reaction. The temperature rise corresponding to the complete polymerisation of a 0·1M-solution of styrene was of the order of 2·5°, depending on the temperature and on the apparatus used.

The Degree of Polymerisation.—The effect of monomer concentration. The dependence of the D.P. on the monomer concentration is shown in Figure 1 for −25°, −60°, and −90°. The results admit of no interpretation other than straight lines through the origin, which proves that in this system chain-breaking reactions with monomer are negligible up to a monomer concentration of 0·3M. The results shown in this Figure were obtained from experiments in which no water was added to the system, and the scatter is probably due mostly to the variations in the quantity of residual water which even careful adherence to a routine cannot eliminate entirely. The D.P. is especially sensitive to the water concentration when this is near zero (see below).

The effect of catalyst concentration. The results in the Tables show that the D.P. is independent of the concentration of titanium tetrachloride at all temperatures. This shows that no species the concentration of which is governed by that of the titanium tetrachloride is acting as chain-breaker.

The effect of water concentration. The relevant results are shown in Figure 2 in the form of a Mayo plot. Consider first the curves A, C, and D. These show a strong dependence of the D.P. on the concentration of added water, and their unusual shape will be discussed below. Curve B shows the same general shape at low water concentration, but beyond $1·6 \times 10^{-4}$M the D.P. seems to become independent of the water concentration. An even greater discrepancy between the earlier results of W. R. L. (lines E and F) and those obtain later by C. J. P. is seen at −60° and −90°. The reason is that, as explained in the Experimental section, W. R. L. broke the water phial at the operating temperature, whereas C. J. P. broke it at about 0° and gave the water time to dissolve before lowering the temperature of the reaction mixture. It is evident that in W. R. L.'s experiments the water from the phial did not participate in the reaction so that the nominal water concentration is really irrelevant, and only the residual water, which had ample time to dissolve, was effective. This is also shown by C. J. P.'s result obtained by W. R. L.'s technique (see Figures 2 and 7; Table 2, Expt. CP17). The practice of introducing ice into a reaction mixture at low temperature is not as absurd as its sounds, since the same technique was being used simultaneously in experiments with isobutene [2] and gave results which showed that with this monomer (and the same catalyst and solvent) the ice reacted instantaneously.

One mystery to which we have not found a solution is that the D.P.s obtained by W. R. L. at −33° are consistently lower than those obtained by C. J. P. at −25°. It may have been that W. R. L.'s reaction mixtures contained a chain-breaking impurity which was absent from, or scarcer in, those of C. J. P.

The effect of temperature. The curves in Figure 2 show the difficulty of obtaining a meaningful variation of D.P. with temperature. However, from the plots in Figure 1 an

TABLE 1

The variation of R_0, $k_2{}^0$, and the D.P. with the monomer concentration

Expt. no.	$[P_1]$	R_0 (deg./min.)	$k_2{}^0$ (l. mole^{-1} sec.$^{-1}$)	D.P.
−25°, $[TiCl_4] = 3·00 \times 10^{-3}$, $[H_2O]$ unknown, constant				
CP2	0·103	3·13	0·148	34·5
CP6	0·112	4·05	0·160	35·1
CP5	0·113	3·91	0·153	35·6
CP1	0·145	6·05	0·145	51·3
CP4	0·176	8·33	0·138	60·1
CP3	0·240	15·2	0·140	—
			Av. = 0·147	
−31°, $[TiCl_4] = 2·29 \times 10^{-3}$, $[H_2O] = 4·16 \times 10^{-4}$				
ST51	0·086	2·66	0·252	—
ST52	0·129	6·85	0·284	—
ST50	0·170	10·70	0·256	—
			Av. = 0·264	
−63° ± 2°, $[TiCl_4] = 2·4 \times 10^{-3}$, $[H_2O]$ unknown, constant				
ST19	0·089	1·70	0·138	68·0
ST20	0·134	3·96	0·143	101
ST7	0·178	7·20	0·141	115
ST22	0·233	12·60	0·148	195
ST21	0·269	11·76	(0·105)	196
			Av. = 0·143	
−91° ± 0·5°, $[TiCl_4] = 2·53 \times 10^{-3}$, $[H_2O]$ unknown, constant				
ST16	0·094	3·84	0·159	140
ST12	0·094	3·84	0·234	118
ST17	0·140	4·90	0·137	220
ST13	0·140	5·00	0·151	210
ST10	0·189	13·0	0·200	287
ST9	0·189	10·0	0·153	284
			Av. = 0·170	

Arrhenius plot for " zero added water " can be constructed. This is shown in Figure 3 and gives an activation energy of D.P., $E_M = -2·1 \pm 0·2$ kcal./mole. Figure 3 also shows a set of individual results (Table 6) obtained with an unknown, probably rather high, water concentration. At the lower temperatures they agree well with those obtained at $[H_2O] = 0$, but they diverge from these increasingly at higher temperatures, as is to be expected. Arrhenius plots for the maxima and minima of curves A, C, and D of Figure 2 also give values of E_M of about -2 kcal./mole.

The Rate of Polymerisation.—The internal order of the reactions. Some forty reaction curves of the ST series were analysed by Wen-Hsuan Chang's method [14] and the order was found to be 1·3 ± 0·3 with no evidence of any systematic trend. On this basis we reported [3] that the internal order was probably unity. However, subsequent analysis by Wilkinson's method [11] of twenty-five curves obtained by C. J. P. gave an order of 2·0 ± 0·05. The discrepancy is most probably due to the greater reliability of the commercial recorder used by C. J. P. and the fact that Wilkinson's method is more accurate than Wen-Hsuan Chang's; we are now confident that the reactions are internally of second order. The only exceptions are those reactions which did not go to completion; the order of all of these was significantly greater than two. The internal second-order rate constants derived from the Wilkinson plots are denoted as k_2'. It will be seen from the Tables that these constants agree very well with the rate constants k_2^0 derived from the initial rates.

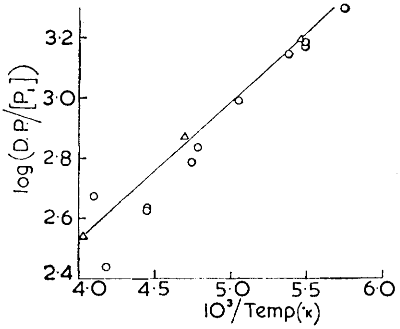

FIGURE 3. The Arrhenius plot for the D.P.
○ Results from Table 6.
△ Results from Figure 1.

The variation of rate with monomer concentration. The results in Table 1 show that at all temperatures the initial rate R_0 is proportional to the square of the monomer concentration:

$$R_0 = k_2^0 [P_1]_0^2$$

TABLE 2

The dependence of R_0, k_2^0, and the D.P. on the catalyst and water concentration at $-25°$

Expt. no.	$[P_1]$	$10^3[TiCl_4]$	$10^4[H_2O]$	R_0 (deg./min.)	k_2^0 (l. mole^{-1} sec.$^{-1}$)	k_2' (l. mole^{-1} sec.$^{-1}$)	D.P.
$[H_2O]$ unknown, but constant: residual after ½ hour's pumping							
CP10	0·163	1·32		7·80	0·145		47·4
CP9	0·163	3·03		7·83	0·147		45·3
CP8	0·163	4·67		7·61	0·143		45·8
*	—	3·00		—	0·147		—
$[TiCl_4] = 3·65 \times 10^{-3}$							
CP15	0·155		†	4·75	—		40·4
CP14	0·156		0·032	6·17	0·159	0·183	60·4
CP13	0·157		0·17	6·82	0·159	0·134	62·8
CP12	0·156		1·17	10·3	0·205	0·256	56·9
CP16	0·170		2·33	21·0	0·338	0·356	56·7
CP18	0·151		5·09	23·4	0·480	0·552	75·0
CP11	0·157		5·53	26·1	0·489	0·579	92·5
CP17 ‡	0·186		5·77	15·0	0·21		56·4

* From Table 1. † Residual $[H_2O]$ after 5 hours' pumping. Reaction stopped at 65% conversion, admission of air induced a second reaction. ‡ Expt. carried out with W.R.L.'s technique (see text).

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[14] Wen-Hsuan Chang, *J. Phys. Chem.*, 1957, **61**, 819.

Table 3

The dependence of R_0, k_2^0, and the D.P. on the concentration of added water at $-33° \pm 1°$

Expt. no.	$10^4[\mathrm{H_2O}]$	R_0 (deg./min.)	k_2^0 (l. mole^{-1} sec.$^{-1}$)	D.P.
ST48	0	8·10	0·195	57
ST49	0·16	9·52	0·229	59
ST46	1·05	10·2	0·247	55
ST47	1·52	10·5	0·252	54
ST50	4·16	10·7	0·256	56

$[\mathrm{P_1}] = 0{\cdot}170$, $[\mathrm{TiCl_4}] = 2{\cdot}28 \times 10^{-3}$.

Table 4

The dependence of R_0, k_2^0, and the D.P. on the concentration of catalyst and of added water at $-60°$

Expt. no.	Temp.	$[\mathrm{P_1}]$	$10^3[\mathrm{TiCl_4}]$	$10^4[\mathrm{H_2O}]$	R_0 (deg./min.)	k_2^0 (l. mole^{-1} sec.$^{-1}$)	k_2' (l. mole^{-1} sec.$^{-1}$)	D.P.
ST27	−63°	0·178	1·20	0 *	2·50	0·050		145
ST26	−63	0·178	2·36	0 *	6·04	0·126		125
ST39	−63	0·178	2·40	0 *	5·30	0·107		141
ST7	−61	0·178	2·45	0 *	7·16	0·141		115
CP23	−60	0·127	2·61	0 *	3·95	0·143	0·151	70·9
ST28	−64	0·178	3·58	0 *	5·94	0·120		138
CP25	−60	0·214	4·12	0 †	15·42	0·228	0·265	117
CP22	−60	0·157	2·61	0·035	5·98	0·139	0·157	119
ST45	−64	0·178	2·40	0·17	6·55	0·132		141
CP21	−60	0·134	2·61	0·18	4·25	0·150	0·156	127
ST42	−64	0·178	2·40	1·11	9·01	0·181		133
CP20	−60	0·131	2·61	1·27	4·18	0·179	0·156	84·5
ST44	−63	0·178	2·40	1·61	8·75	0·176		141
CP24	−60	0·183	3·89	2·50	7·53	0·224	0·200	106
ST41	−63	0·178	2·40	4·90	8·81	0·183		142
CP19	−60	0·130	2·16	6·01	4·89	0·148	0·147	138

* After 5 hours' pumping. † After ½ hour's pumping.

Table 5

The dependence of R_0, k_2^0, and the D.P. on the concentration of catalyst and of added water at $-90°$

Expt. no.	Temp.	$[\mathrm{P_1}]$	$10^3[\mathrm{TiCl_4}]$	$10^4[\mathrm{H_2O}]$	R_0 (deg./min.)	k_2^0 (l. mole^{-1} sec.$^{-1}$)	k_2' (l. mole^{-1} sec.$^{-1}$)	D.P.
CP35	−90°	0·301	0·53	0 †	5·52	0·037	0·028	508
ST54	−91	0·188	1·18	5·15	5·16	0·083		320
ST31	−92	0·188	1·27	0 *	3·16	0·040		—
ST32	−92	0·188	1·89	0 *	2·50	0·039		355
CP30	−90	0·231	1·41	0 *	10·6	0·117	0·117	330
CP29	−90	0·236	1·41	0·037	9·33	0·117	0·113	371
CP28	−90	0·244	1·41	0·20	7·49	0·108	0·117	388
CP27	−90	0·276	1·41	1·36	15·0	0·116	0·116	353
CP26	−90	0·273	1·41	2·72	9·31	0·108	0·117	450
CP31	−90	0·228	1·41	6·42	6·83	0·112	0·115	465
CP34	−90	0·292	1·60	0 †	13·5	0·109	0·093	440
ST34	−91	0·188	2·51	0 *	3·86	0·060		320
ST35	−92	0·188	2·51	0 *	3·64	0·057		354
ST38	−92	0·188	2·51	0·52	4·52	0·070		341
ST36	−91	0·188	2·51	1·16	8·75	0·135		341
ST43	−91	0·188	2·51	1·67	11·4	0·180		344
ST37	−91	0·188	2·51	5·15	11·0	0·172		331
CP32	−90	0·264	2·64	0 †	17·1	0·173	0·163	440
CP33	−90	0·270	2·66	0 *	19·5	0·171	0·177	402
ST53	−92	0·188	3·73	5·15	14·8	0·233		340

* After 5 hours' pumping. † After ½ hour's pumping.

TABLE 6

The dependence of R_0, k_2^0, and D.P. on temperature

Expt. no.	Temp.	$[P_1]$	$10^3[TiCl_4]$	R_0 (deg./min.)	k_2^0 (l. mole^{-1} sec.$^{-1}$)	D.P.
ST4	−28·7°	0·170	2·20	6·96	0·167	83·9
ST1	−30·2	0·171	2·33	6·82	0·162	—
ST11	−33·2	0·173	2·33	6·32	0·202	47·6
ST6	−48·4	0·176	2·38	5·50	0·116	74·6
ST5	−49·0	0·177	2·39	6·76	0·145	75·7
ST7	−61·2	0·181	2·45	7·16	0·142	110
ST26	−63·4	0·176	2·36	6·04	0·126	120
ST8	−75·3	0·184	2·49	9·14	0·164	177
ST23	−86·7	0·185	2·49	10·10	0·167	262
ST9	−91·4	0·189	2·55	10·00	0·152	284
ST10	−91·5	0·189	2·55	13·00	0·199	287
ST24	−99·1	0·193	2·59	14·10	0·191	383

In the experiments recorded in this Table the water concentration was unknown, but constant and probably relatively great.

The variation of rate with catalyst concentration. At −25° and constant $[H_2O]$ the rate and k_2^0 are independent of the concentration of titanium tetrachloride between 1·32 and 3·00 mmole/l. (Table 2); presumably there must be an increase of rate from zero at lower catalyst concentrations.

At −60° (Table 4 and Figure 4) k_2^0 increases with the catalyst concentration. Whilst a rectilinear dependence is not excluded, a sigmoid curve seems more likely. All the results plotted were obtained with $[H_2O] > 10^{-4}$M, *i.e.*, in the region in which k_2^0 is independent of $[H_2O]$ (see Figure 7).

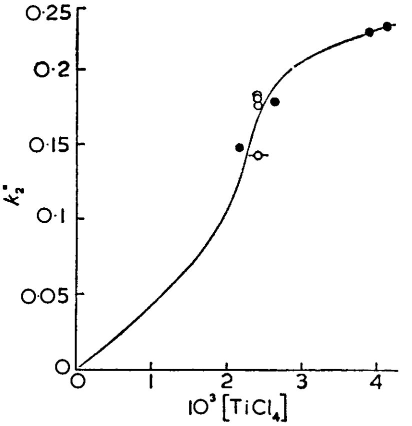

FIGURE 4

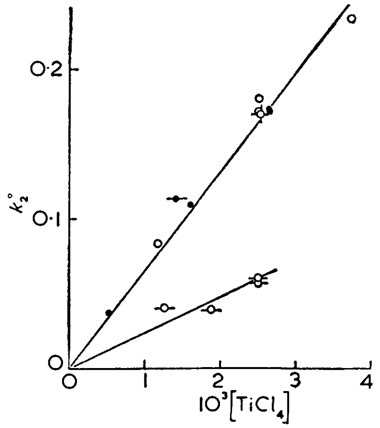

FIGURE 5

FIGURE 4. The variation of k_2^0 with $[TiCl_4]$ at −60°. For all points shown $[H_2O] > 10^{-4}$ (see Table 4)
○ W. R. L. ● C. J. P. —○— from Table 1 (W. R. L.)

FIGURE 5. The variation of k_2^0 with $[TiCl_4]$ at −90° (see Table 5)
—○—W. R. L. $[H_2O] = 0$, *i.e.*, residual. ○ W. R. L. $[H_2O] > 1·67 \times 10^{-4}$.
● C. J. P. $[H_2O]$, various (see Table 5). —⦶— W. R. L., derived from Table 1.
—●— C. J. P. from Figure 9.

At −90° (Table 5 and Figure 5) k_2^0 increases rectilinearly with $[TiCl_4]$. The fact that W. R. L.'s results with only residual water fall on a line which is different from that through all the other results will be discussed below.

The variation of rate with water concentration. When C. J. P. repeated W. R. L.'s experiments in the −30° region, the discrepant results shown in Figure 6 were obtained, but when he used W. R. L.'s technique of breaking the water phial at the working temperature (see Experimental section), the specially marked point in Figure 6 resulted, which showed that the discrepancy was due to the difference in technique. It appears that in these experiments, in contrast with those with isobutene,[2] ice does not react appreciably at −25° or below. Thus, for W. R. L.'s experiments the nominal water concentration is really irrelevant, the real water concentration being that due to the residual water, and the results show how closely reproducible this was.

At −60° and −90° (Figures 7 and 8) k_2^0 rises to a constant value at quite low concentrations of added water $[H_2O]$. Whether the constancy of the rate beyond this point is a chemical effect, or a trivial physical one (saturation) is not immediately obvious. A comparison with the variation of the D.P. with $[H_2O]$ (Figure 2) suggests that at −60° the effect is chemical, since the D.P. does vary (for C. J. P.'s results) with the water concentration. The same conclusion applies to C. J. P.'s results at −90°; the concentration of water affects (slightly) the concentration of chain-breaking species in the solution, but does not affect the reaction rate.

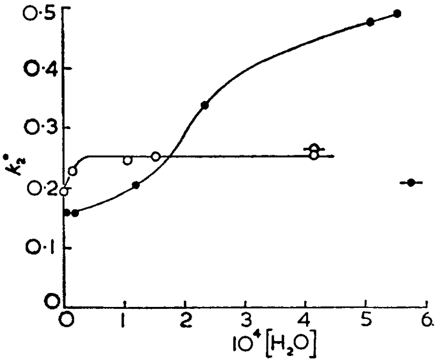

FIGURE 6. The variation of k_2^0 with $[H_2O]$ (see Tables 2 and 3)

○ −33°, W. R. L. ● −25°, C. J. P. —●— −25°, C. J. P. using W. R. L.'s technique (see text). —○— −31°, W. R. L., derived from Table 1.

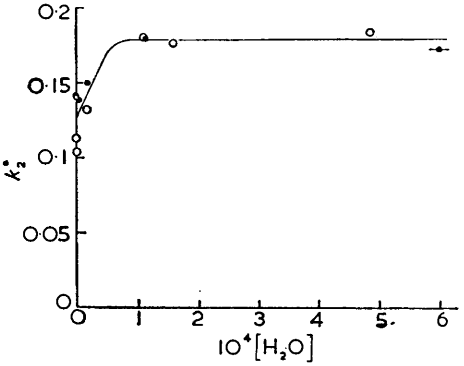

FIGURE 7

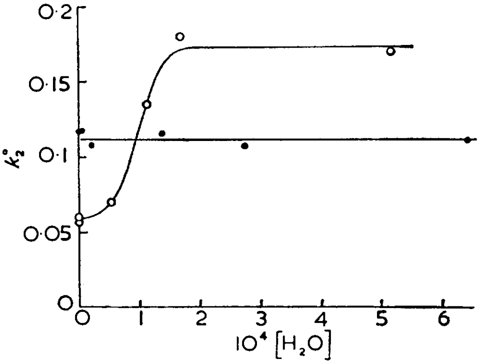

FIGURE 8

FIGURE 7. The variation of k_2^0 with $[H_2O]$ at −60° (see Table 4)

○ $[TiCl_4] = 2{\cdot}4 \times 10^{-3}$ (W. R. L.). ● $[TiCl_4] = 2{\cdot}6 \times 10^{-3}$ (C. J. P.).
—●— $[TiCl_4] = 2{\cdot}16 \times 10^{-3}$, k_2^0 plotted is the experimental value × 2·5/2·16.

FIGURE 8. The variation of k_2^0 with the concentration of added water at −90° (see Table 5)

○ $[TiCl_4] = 2{\cdot}51 \times 10^{-3}$ (W. R. L.). ● $[TiCl_4] = 1{\cdot}41 \times 10^{-3}$ (C. J. P.)

The results of W. R. L. at −90° present an unresolved enigma: they show that at " zero added water " the slope of the line relating k_2^0 to $[TiCl_4]$ is much smaller than at all other water concentrations (Figure 5), and differ in this respect from C. J. P.'s results; they show a dependence of k_2^0 on $[H_2O]$, in contrast with C. J. P.'s results (Figure 8); yet the addition of water during a run (see below) did not affect the rate. We must conclude that W. R. L.'s experiments at the lowest water concentrations were affected by an unknown factor, and they will be ignored in the subsequent discussion.

At all temperatures the k_2^0 at zero added water is so great that it suggests the intervention of a reaction which is independent of co-catalysis by water. Further, if one assumes that the water-co-catalysed reaction is the only one, back extrapolation of the rising branch of the curves in Figures 6—8 to $k_2^0 = 0$ should give the concentration of residual water. The values thus obtained are so high, compared with those obtained by the same method for the same apparatus, procedure, and reagents with isobutene,[2] that this also suggests the existence of a reaction the rate of which is independent of the water concentration.

Exploratory Experiments.—An experiment which was repeated many times by W. R. L. and C. J. P. was the addition of water during a polymerisation at $-90°$. In one version the apparatus was opened to the air, in another a phial of water was broken. It was always found that this procedure had no effect whatever on the rate of the polymerisation. This is in strong contrast with our experience with isobutene, with the same catalyst and solvent; with this monomer there would have been a marked acceleration.

Since the experiments quoted above and the kinetic evidence suggested that at low temperatures there might be a polymerisation which did not require water, the following experiment was carried out.

Styrene was polymerised at $-25°$ in the absence of added water in an apparatus that had been previously flushed several times with trimethylchlorosilane vapour to minimise the concentration of residual water. The reaction curve showed that the reaction had gone to about 30% conversion, and presumably all available water in the system was used up by this reaction. When the reaction trace showed that the reaction had ceased, the temperature of the mixture was rapidly lowered to $-90°$, and kept there for a few minutes. With decreasing temperature the originally pale yellow colour of the solution became much deeper. The weight of the precipitated polymer showed that the reaction had gone to 100% conversion. Thus, 70% of the monomer must have been polymerised in the absence of water.

The large value of k_2^0 at $[H_2O] = 0$ in Figure 7 suggested that the suspected reaction which is independent of water also existed at $-25°$, but that it was largely swamped by the reaction co-catalysed by water. To test this idea, styrene was polymerised without added water at $-25°$. The reaction apparently stopped at about 40% conversion, having presumably consumed the residual water. The reaction mixture was then left under vacuum for 1 hr. at $-25° \pm 1°$. At the end of this period, the catalyst was destroyed by admitting methanol vapour (and not air, the moisture in which could have caused further reaction) into the reaction vessel and stirring the mixture for 15 min. The weight of recovered polymer showed that the reaction had gone to 80% conversion. Thus, if the first reaction had consumed all available water then the polymer formed subsequently must have originated from a reaction that did not require water.

DISCUSSION

The Nature of the Chain-carriers.—Until the middle of 1964 it was generally believed that in polymerisations catalysed by acids or metal halide–co-catalyst complexes the chain-carriers are carbonium ions. Then Gandini and Plesch [15] showed that in the polymerisation of styrene by various acids or by stannic chloride and water at *ca.* 20° the chain-carriers are not ions, but are most probably esters. There is some evidence that for catalysis by titanium tetrachloride and water the same is true, but the range of temperatures and concentrations relevant to the present study has not yet been explored from this point of view. Therefore, in order not to prejudge the issue, the chain carriers will be designated below by P_n^*, and we will scrutinise our results for evidence concerning their nature.

The yellow colour of the polymerising solutions, which is deceptively similar to " carbonium-ion yellow," is at least partly (possibly entirely) due to the tail of a peak in the near ultraviolet which is caused by the complexes between titanium tetrachloride and styrene and/or polystyrene.[16]

The Kinetic Character of the Polymerisation.—In our results there is no evidence

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[15] A. Gandini and P. H. Plesch, *Proc. Chem. Soc.*, **1964**, 240; *J. Polymer Sci., Part B, Polymer Letters*, 1965, **3**, 127.

[16] W. R. Longworth, unpublished work; A. Gandini and P. H. Plesch, unpublished work.

suggesting that the propagation is anything other than a normal bimolecular reaction between growing chains and monomer; hence

$$V_p = k_p\,[P_1]\,[P_n^*].$$

Since the D.P. is greater than 30 at all temperatures, monomer consumption by processes other than propagation can be neglected, and hence the reaction rate $R = V_p$. Since the internal order and the external order with respect to monomer are both two, and the rate constants are identical, $k_2^0 = k_2' \equiv k_2$, it follows that

$$V_p = k_2\,[P_1]^2$$

and therefore

$$k_p\,[P_n^*] = k_2\,[P_1].$$

It also follows that the reactions are stationary, *i.e.*, $[P_n^*]$ is constant, for, if it were not, the internal order would be greater than two; this situation was indeed found for those few reactions which, for lack of water, did not go to completion—the concentration of chain carriers, $[P_n^*]$, diminished to zero before all the monomer had been consumed.

In the stationary reactions the stationary state cannot be of the Second Kind ($V_i = V_t = 0$), in which [17] $V_p = k_1\,[P_1]$, and it must therefore be of the First Kind ($V_i = V_t \neq 0$). The simplest assumptions about a system of this type which will give the required kinetics are that

$$V_i = k_i\,[P_1]\,[X]$$

where X is the initiating species, and

$$V_t = k_t\,[P_n^*],$$

whence it follows that

$$V_p = k_i k_p\,[P_1]^2[X]/k_t,$$

and that

$$k_2 = k_i k_p\,[X]/k_t$$

The experimentally determined dependences of k_2 on the concentrations of titanium tetrachloride and water, and their variations with temperature, thus reflect the chemistry of the initiation process and possibly also the varying abundance of different kinds of propagating species.

The dependence of k_2 on $[TiCl_4]$ can be rationalised as follows: the results in Table 2 and Figure 4 show that provided $[H_2O]$ exceeds a certain value, k_2 increases with $[TiCl_4]$ up to a maximum value which then remains constant. The value of $[TiCl_4]$ at which k_2 becomes constant increases as the temperature is reduced; it is less than $1{\cdot}3 \times 10^{-3}$ at $-25°$ and about 4×10^{-3} at $-60°$. At $-90°$ (Figure 5) k_2 increases rectilinearly with $[TiCl_4]$ and if it does become independent of $[TiCl_4]$, this must occur at a concentration considerably greater than 4×10^{-3}

The variation of k_2 with $[H_2O]$ shows a similar behaviour, but the limiting concentration moves in the opposite direction (Figures 6—8). At $-25°$ k_2 becomes independent of $[H_2O]$ at about 5×10^{-4}, at $-60°$ at about 1×10^{-4}, and at $-90°$ it is independent from $[H_2O] = 0$. Moreover, the magnitude of the effect of the water concentration decreases with decreasing temperature to zero at $-90°$, and all the evidence indicates the existence of a polymerisation reaction which is independent of the presence of water. In other words, k_2 is finite at $[H_2O] = 0$ and, at temperatures above $-90°$, rises over a small range of water concentrations beyond which it is once again independent of $[H_2O]$.

From the purely algebraic point of view all the results can be represented by an equation of the form

$$k_2 = \frac{A\,[TiCl_4]\,[H_2O]^m}{1 + B\,[H_2O]^m} + \frac{\alpha[TiCl_4]^n}{1 + \beta[TiCl_4]^n}$$

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[17] D. C. Pepper and P. J. Reilly, *J. Polymer Sci.*, 1962, **58**, 639.

where A, B, α, β are temperature-dependent constants, and m, $n \geqslant 1$ and vary with temperature. The shapes of the curves suggest that equilibria are involved in the initiation reactions and this is expressed by this equation which is of a form familiar in the chemistry of equilibria. However, since the constants involved cannot be interpreted at present, their evaluation from our results is not useful at this stage. Further, since k_2 is composite, no meaningful activation energy can be derived from our results.

Whilst the details of the initiation remain regrettably obscure, the results do show very clearly that two quite separate initiation mechanisms operate simultaneously, one involving water and strongly dependent on temperature, the other independent of water and dominant at the lower temperatures. If, as seems very likely, the resulting chain-carriers are different, we have here another instance of enieidic polymerisation,[2,18] *i.e.*, one in which more than one species of chain-carrier coexist in the same system.

The present results contain no features which could indicate a change in the relative abundance of free ions and ion-pairs with temperature, such as is very evident in the polymerisation of isobutene under the same conditions. This is one indication that the chain-carriers are not ionic. The large normal temperature coefficient of the water-co-catalysed reaction also suggests that this, at least, is not ionic. We therefore conclude, very tentatively, that the chain-carriers in this reaction are more likely to be of the ester type than ionic. However, the whole matter is so uncertain that the formulation of mechanisms for initiation, etc., is not worth while.

The Degree of Polymerisation.—In the Results section we explained that in the present system there is no evidence for chain-breaking by monomer transfer, or by reaction with any species the concentration of which is governed by that of titanium tetrachloride. The only evidence on chain-breaking reactions comes from the kinetics, which indicate the existence of a unimolecular termination, and from the dependence of the D.P. on the water concentration.

The variation of the D.P. with the water concentration can be interpreted by Plesch's theory.[19] According to this the maxima in the D.P.s (minima in Figure 2) mean that in our reaction mixtures there was a chain-breaking impurity G at a concentration of the order 3×10^{-5} M which reacts with water to give a product H which is either not a chain-breaker, or is a much less effective one than G. The very low concentration of this chain-breaker G makes it impossible to identify it and unprofitable to speculate on its nature, but it is notable that it appears in both series of experiments.

A further increase in the water concentration leads to the formation of a new chain-breaker, say H′, the maximum concentration of which is of the order 2×10^{-4} M. When the water concentration is increased beyond this, the D.P. rises again, which shows that H′ is being transformed by reaction with water to products which are relatively ineffective chain-breakers.

The minima and maxima in Figure 2 are in no way correlated with features in the corresponding plots of k_2^0, which indicates that the chain-breakers removed by, or formed from, water cannot be terminators and must therefore be transfer agents.

Since the peculiar dependence of the D.P. on the water concentration seems to be determined by a trace impurity, experiments with other solvents, or with styrene of different origin, or purified differently, may give results at variance with ours.

CONCLUSION

The results presented above are among the most reproducible and consistent ones which have been obtained in this difficult field, and the range of conditions which has been explored is wide. It is therefore particularly disappointing that the chemical information

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[18] Chapter on Cationic Polymerisation by P. H. Plesch in " Progress in High Polymers," vol. 2, ed. J. C. Robb and F. W. Peaker, Heywood and Co., London, in the press.

[19] P. H. Plesch, *J.*, **1964**, 104.

which they have yielded is so meagre. Perhaps the most significant point to emerge is that, with the same catalyst, co-catalyst, and solvent, the polymerisations of styrene and isobutene are utterly different in almost every respect, and we conclude that they may in fact be different types of reaction. This conclusion will make the interpretation of co-polymerisation experiments even more than usually difficult and hazardous. We conclude further that kinetic studies are not the most suitable for investigating these systems, and that other approaches, *e.g.*, through spectroscopy, are likely to yield more significant chemical information with less effort.

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