42. *The Low-temperature Polymerisation of Isobutene. Part VI.*[1] *Polymerisation by Titanium Tetrachloride and Water in Methylene Dichloride.*

By R. H. Biddulph, P. H. Plesch, and P. P. Rutherford.

The polymerisation of isobutene in methylene dichloride by titanium tetrachloride, with water as co-catalyst, has been studied in the temperature range +18° to −91° by a rigorous high-vacuum technique. Rates, kinetic orders, degrees of polymerisation, and yields have been obtained as a function of the concentrations of all three reagents over the whole temperature range. The results, which are complicated, indicate that a co-catalyst, such as water, is necessary in this system, and that the character of the reaction changes with temperature. Our findings are interpreted by the theory that at the higher temperatures the polymerisation is propagated by ion-pairs, and that at the lower temperatures propagation by free ions is dominant. Some of the implications of this theory are confirmed by the results of other workers.

This investigation of the polymerisation of isobutene by titanium tetrachloride was started in 1954 with exploratory work during which the experimental technique was perfected [2a] and which led to the choice of methylene dichloride as solvent.[2b] At the time, analogy with related systems [3,4] gave good reason to believe that methylene dichloride could act as co-catalyst to titanium tetrachloride in the polymerisation of isobutene, and the degree of reproducibility of rates and degrees of polymerisation (D.P.) at first appeared to confirm this view. However, a numer of polymerisations did not go to completion and a detailed investigation then showed that the solvent is not a co-catalyst and that a co-catalyst such as water is required. In this Paper we report studies of the effect of the reagent concentrations on the kinetics of the polymerisation and on the yield and D.P. of the polymers prepared under rigorously defined conditions over the temperature range +18° to −91°. Some of these results have been reported briefly.[2a,5,6] Where the information given in this Paper differs from that in the earlier publications, the latter are superseded.

Experimental

Materials.—Isobutene was purified as already described [2a,b] and stored over colloidal sodium in a reservoir attached to the reaction apparatus. Methylene dichloride, purified as described earlier,[7] was stored over calcium hydride in the reservoir, and was refluxed and out-gassed intermittently for at least a week before use. Titanium tetrachloride was purified [7] and solutions in methylene dichloride were made up and sealed into phials as already described.[2c]

Phials containing known quantities of water were prepared as follows. Distilled water was out-gassed on a vacuum manifold, and a middle fraction was distilled into a reservoir of about 50-ml. capacity. This was attached to a vacuum manifold comprising the glass phials and a dosing bulb of 40·5-ml. capacity. The dosing bulb, manifold, and phials were made hydrophobic by chlorotrimethylsilane vapour. To fill a phial, the reservoir was surrounded by a bath at a known temperature, and the dosing bulb was filled with water vapour; its contents were condensed into the phial, and this was then sealed off. The quantity of water was computed from the water-vapour pressure and the volume of the dosing bulb. The use of the vapour of

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[1] Part V, Beard, Plesch, and Rutherford, *J.*, 1964, 2566.

[2] (*a*) Biddulph and Plesch, *Chem. and Ind.*, 1959, 1482; (*b*) *J.*, 1960, 3913; (*c*) *Chem. and Ind.*, 1956, 567.

[3] Fontana and Kidder, *J. Amer. Chem. Soc.*, 1948, **70**, 3745; " Cationic Polymerisation and Related Complexes," ed. Plesch, Heffer and Co., Cambridge, 1953, p. 121.

[4] Pepper, *Trans. Faraday Soc.*, 1949, **45**, 397.

[5] Biddulph, Plesch, and Rutherford, Symposium on Macromolecules, Wiesbaden, 1959, Paper IIIA10.

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

[7] Longworth, Plesch, and Rigbi, *J.*, 1958, 451.

ice at temperatures below 0° enabled us to handle extremely small quantities of water. The reliability of the method was checked by weighing.

Apparatus and Procedure.—The reaction apparatus with its attached reservoirs for monomer and solvent, and the operating routine, have been described in detail.[2a] The reactions were followed in an adiabatic calorimeter with a temperature recorder. The rate and the extent of reaction were obtained from the reaction curves drawn by the recorder. Examples of typical reaction curves are shown in Figs. 1 and 2. From the speed of movement of the chart and the calibration of the platinum resistance thermometer, the initial rate of reaction was determined. The apparent initial rate of each reaction (in deg. min.$^{-1}$) was determined from the slope of the tangent to the initial part of the time–temperature curve. To obtain the true initial rate of reaction, tabulated as R_i, the rate of spontaneous cooling before the reaction, which was always kept very low, was added algebraically to the apparent reaction rate to allow for heat loss during the reaction.

To obtain the true concentrations of the reagents the volume of the solutions at the operating temperature was computed from the volume of solvent measured at room temperature and the density of methylene dichloride at the relevant temperature.*

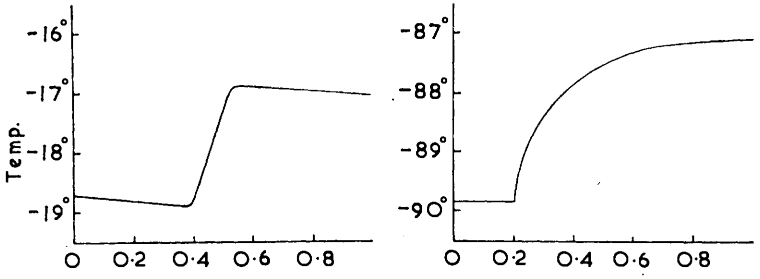

FIG. 1. FIG. 2.

Typical reaction curves obtained for polymerisation. FIG. 1, Above −30°. FIG. 2, Below −60°.

The technique of experimentation was very tedious because, even when the whole apparatus had been rendered hydrophobic as described above, many hours of pumping at about 10^{-5} mm. were required to reduce the level of residual water to such an extent that the effects of an " insufficiency " of water could be detected and studied. Since the efficacy of water rises very markedly as the temperature is reduced, it became increasingly difficult to attain sub-critical water levels.

The rate constant, k_1, shown in the following Figs. is defined by the relation

$$R_i = k_1[P_1]_0 \qquad (1)$$

where $[P_1]_0$ is the initial monomer concentration. The units of k_1 are l. deg. min.$^{-1}$ mole^{-1}. The conversion factor, F, to absolute units, *i.e.*, min.$^{-1}$, was obtained by an electrical calibration involving measurement of the heat capacity of the system over the whole temperature range, and measurement of the heat of polymerisation of isobutene.[10] This conversion factor is given by the equations

$$k_1' \text{ (min.}^{-1}\text{)} = Fk_1; \quad F = 4{\cdot}66 \times 10^{-2} + 9{\cdot}4 \times 10^{-5}t \ (t \text{ in } {}^\circ\text{c})$$

The order of the reactions was calculated from the ratios of the quarter-, half-, and three-quarter-lives by Wen-hsuan Chang's method.[11]

The yield of any incomplete reaction ($Y\%$) was obtained by comparing the temperature rise

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* The coefficient of expansion given by Weissberger [8] is evidently a misprint; the correct value [9] is $1{\cdot}78 \times 10^{-3}$.

[8] " Techniques of Organic Chemistry," ed. Weissberger, Vol. VII, 2nd edn., Interscience Publ., Inc., New York, 1955.

[9] Morgan and Lowry, *J. Phys. Chem.*, 1930, **34**, 2385.

[10] Biddulph, Longworth, Penfold, Plesch, and Rutherford, *Polymer*, 1960, **1**, 521.

[11] Wen-hsuan Chang, *J. Phys. Chem.*, 1957, **61**, 819.

for the particular polymerisation with that obtained under identical conditions with an excess of water to ensure complete reaction, since, as will be shown below, the yield depended critically on the prevalent water concentration. This relation was so reliable that for many reactions carried out with " residual water " only, *i.e.*, with the water remaining in the system after evacuation, the quantity of this water could be estimated from the yield of polymer. The reliability of the estimates of yield obtained from the temperature rises was repeatedly checked by weighing the polymer obtained.

Chlorine Analyses.—Some of the polymers were purified by several precipitation–solution cycles (ethanol and hexane) and analysed for chlorine at the Thornton Research Centre of Shell Research Ltd.

Determination of Molecular Weight.—The molecular weight of polymers was calculated from the intrinsic viscosity of di-isobutene solutions at 25°, by the use of Flory's constants.[12] Consequently the D.P.'s in this Paper are viscosity-average values. Number-average D.P.'s will be denoted by $\text{D.P.}_{\cdot n}$.

Infrared Spectra.—The infrared spectra of whole polymers and of fractions obtained in the course of molecular-weight fractionations [13] were recorded with a Perkin-Elmer Infracord instrument. For reference the spectra of " di-isobutene " (a mixture of the 1-ene and 2-ene isomers) and of polyisobutene of D.P. $>20,000$ were used.

Reproducibility.—The results obtained by R. H. B. and P. P. R. during five years with many batches of reagents agree very closely. However, the results as a whole, especially those obtained at the lower temperatures, show a relatively large scatter, which makes the exact nature of some of the correlations rather uncertain. This we attribute in part to defects in our home-made recorder, to lack of control of the extremely small quantities of water involved in many of the reactions, and to the possible presence of impurities of unknown origin.

Because of operational difficulties the initial temperatures quoted are means, with a variation of $\pm 2°$ between experiments in any one temperature group.

RESULTS

Appearance of the Reaction Mixtures.—The reaction mixtures and the polymers were colourless. Since polyisobutenes of $M >$ *ca.* 30,000 are insoluble in methylene dichloride, and since the molecular weight increases as the temperature of reaction decreases, the polymers obtained at temperatures below about $-15°$ came out of solution as tacky gels, the appearance of which —white fibrous, or translucent—depended on the temperature and on the isobutene and water concentrations.

Properties of the Polyisobutenes.—*Chlorine content.* The chlorine content of all the polymers analysed is shown in Table 1.

TABLE 1.

Chlorine content of some polyisobutenes of low molecular weight.

Expt. no.	T_i *	$[\text{TiCl}_4]$ (10^3 mole/l.)	Isobutene (10^2 mole/l.)	10^{-2} D.P.	Cl (%)
107	−12·3°	2·20	8·9	2·84	0·03
66	−12·3	2·20	8·9	3·72	<0·01
80	+3·6	2·15	8·7	1·13	~0·10
132	+17·2	1·58	37·0	2·61	0·04
131	+17·4	1·58	37·0	2·63	0·05
129	+18·2	1·05	37·0	1·37	<0·01
130	+18·4	3·16	37·0	1·36	0·08

* T_i is the initial temperature.

Fractionation of the polymers. The fractionation of some of the polymers obtained in this work has been described by Panton, Plesch, and Rutherford,[13] who obtained D.P. distribution curves of polymers of molecular weight up to 10^6.

Infrared Spectra.—The infrared spectra of polyisobutenes of D.P. $<$ *ca.* 1000 showed the presence of terminal unsaturation, consisting of both vinylidene groups and trisubstituted double bonds.

A prominent feature of all the spectra was the presence of a band at 3400 cm.$^{-1}$, indicating

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[12] Flory, *J. Amer. Chem. Soc.*, 1943, **65**, 771.

[13] Panton, Plesch, and Rutherford, *J.*, 1964, 2586.

hydroxyl groups. For the lowest polymers this was confirmed by a band near 1150 cm.$^{-1}$ (tertiary OH) which is otherwise difficult to detect as it coincides with one of the polymer bands. Some of the spectra showed bands at 2750 and 1730 cm.$^{-1}$, which are due to aldehyde groups. It could be shown that these are artefacts due to atmospheric oxidation of double bonds during evaporation of the polymer solutions at about 70° to form films.

A comparison of the spectra of the second (D.P. 327) and seventh (D.P. 1350) fractions obtained from the fractionation of one polyisobutene (No. 31) showed that the bands at 1360, 1390, and 1470 cm.$^{-1}$ are very sharp for the high polymer, but much broader for the lower polymer. This suggests that certain hydrocarbon groups are relatively more abundant in the oligomer than in the polymer. These could be initial t-butyl groups formed in the initiation or monomer transfer reactions, and $Cl{\cdot}CH_2{\cdot}CH_2$– groups due to solvent transfer.

Effect of Water on Extent of Reaction.—The extent of reaction, Y%, is one of the variables most sensitive to the concentration of water; the dependence of Y on the concentration of water at various temperatures is shown in Figs. 3A and B. From these curves the quantity of residual water in the apparatus and the reagents could be estimated. The residual water, given by the intercept, amounts to about 10^{-6} mole throughout the temperature range +18° to −61°. Since the volume of the reaction mixture was ~100 ml., the concentration of residual water was of the order of 10^{-5} mole/l. At −35° a series of experiments with titanium tetrachloride concentrations of $1{\cdot}27 \times 10^{-3}$ and $2{\cdot}54 \times 10^{-3}$ mole/l., gave essentially the same value for the quantity of residual water.

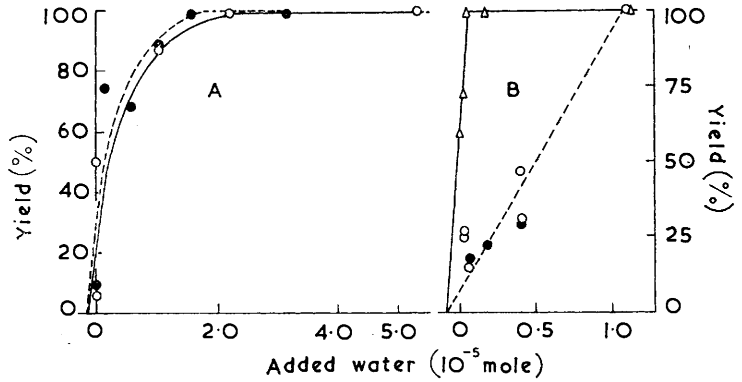

FIG. 3. Dependence of the yield, Y, on the quantity of added water at various temperatures.

(A) [Isobutene] = (0·085—0·096) mole/l.; $[TiCl_4]$ = 2·15 mmole/l. at +5° (●); $[TiCl_4]$ = 2·10 mmole/l. at +18° (○).

(B) [Isobutene] = (0·085—0·096) mole/l.; $[TiCl_4]$ = 1·27 (●) and 2·54 (○) mmole/l. at −35°; $[TiCl_4]$ = 2·37 mmole/l. (△) at T = −61°.

The water concentration just sufficient to give $Y = 100\%$ will be denoted by $[H_2O]_c$. Values of $[H_2O]_c$ at different temperatures are shown in Table 2. The phrase "excess water" is used below to denote $[H_2O] > [H_2O]_c$.

TABLE 2.

The variation of the critical water concentration with temperature.

[Isobutene] = 85—96 mmole/l., $[TiCl_4]$ = 2·1—2·5 mmole/l.

T_i *	+18°	+5°	−14°	−35°	−61°
$[H_2O]_c$ (10^4 mole/l.)	2·1	1·63	1·26	1·19	0·16

* See footnote to Table 1.

Table 3 shows that, when $[H_2O] < [H_2O]_c$, a given quantity of water will polymerise more monomer at high monomer concentrations than at low monomer concentrations.

Mixing Sequence and Reaction Pattern.—In most experiments the phial containing the water was placed in the top position, so that it would be broken first, and that containing the titanium

TABLE 3.

The effect of the concentration of isobutene on the yield.

T_i*	−13°		−60°	
$[H_2O]$ (10^5 mole/l.)	12·5		*ca.* 1·0	
[Isobutene] (mole/l.)	0·090	0·387	0·096	0·436
Y (%)	100 †	86	60, 73	82, 78

In all experiments quoted, $[TiCl_4]$ = 1·24 mmole/l.

* See footnote to Table 1. † For this experiment, $[H_2O]$ was very near to $[H_2O]_c$, so that this result is meaningful in the context of this Table.

tetrachloride in the lower position. A fixed time was allowed for the water to dissolve, and after this the titanium tetrachloride phial was broken. In other experiments both phials were broken by the same drop of the breaker, *i.e.*, virtually simultaneously. Both procedures gave the same shape of reaction curve, and the same reaction rate and molecular weight of polymer. In yet other experiments the titanium tetrachloride phial was broken first, so that an immediate reaction due to the residual water ensued. After this had subsided, the water phial was broken. The shape of the reaction curve and the rate of the second reaction corresponded closely with what was expected from the concentration of titanium tetrachloride, water, and unchanged isobutene. These results show that the rate of dissolution of the water, and its solubility in the reaction mixtures, cannot have been important factors determining the reaction pattern.

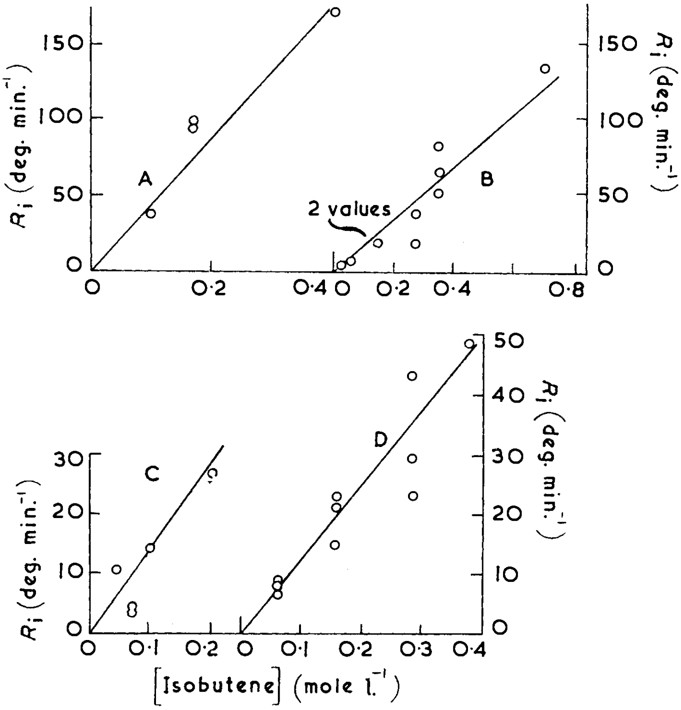

FIG. 4. Variation of the initial rate, R_i, with the concentration of isobutene at various temperatures. $[H_2O] > [H_2O]_c$ for all experiments.

$[TiCl_4]$ = (A) 1·10 mmole/l. at −14°; (B) 0·80 mmole/l. at −35°; (C) 1·8—1·9 mmole/l. at −61°; (D) 0·847 mmole/l. at −91°.

Rate of Reaction at $[H_2O] > [H_2O]_c$.—*Effect of concentration of monomer.* The effect of the concentration of isobutene on the initial rate of reaction, R_i, is shown in Fig. 4: R_i increases linearly with the concentration of isobutene, so that equation (1) is valid up to at least −30°. At temperatures above −14° R_i was so great that the linearity of its variation with the concentration of isobutene is somewhat uncertain.

The shape of the reaction curves depended on the temperature. Below about $-60°$ the curves correspond to first-order reactions; above about $-60°$ the initial part is rectilinear, and the final part is of first-order type, the proportion of the rectilinear part increasing with increasing temperature; and above about $-30°$ the "curves" are entirely rectilinear, the reactions ceasing almost abruptly (Figs. 1 and 2). The change in the shape of the reaction curves (internal order) from zero-order type at the higher temperatures to a pure first-order type at the lowest (Table 4) is gradual, and is a most striking phenomenon. A very short-lived initial acceleration was found only at $-90°$ at extremely low water concentrations, and in a few reactions at the highest temperatures.

TABLE 4.

The variation of the internal order of reaction with temperature for $[H_2O] > [H_2O]_C$.

	Order of reaction obtained from				Order of reaction obtained from		
T_i *	$t_{1/4}/t_{1/2}$	$t_{1/2}/t_{3/4}$	No. of expts.	T_i *	$t_{1/4}/t_{1/2}$	$t_{1/2}/t_{3/4}$	No. of expts.
+18°	0	0	5	−35°	0·1	0·2	15
+5	0·1	0·4	6	−61	0·1	0·8	8
−14	0	0	12	−91	1·0	1·1	17

* See footnote to Table 1.

Effect of catalyst concentration. The variation of k_1 with the concentration of titanium tetrachloride at various temperatures is shown in Fig. 5. Most of the results shown there were obtained with relatively high, but unknown, water concentrations. The curves all appear to have approximately the same shape. However, in view of the scatter of the results, an interpretation different from the curves shown is also possible. The limiting value of k_1 at high titanium-tetrachloride concentrations varies with temperature in the manner shown in Fig. 6.

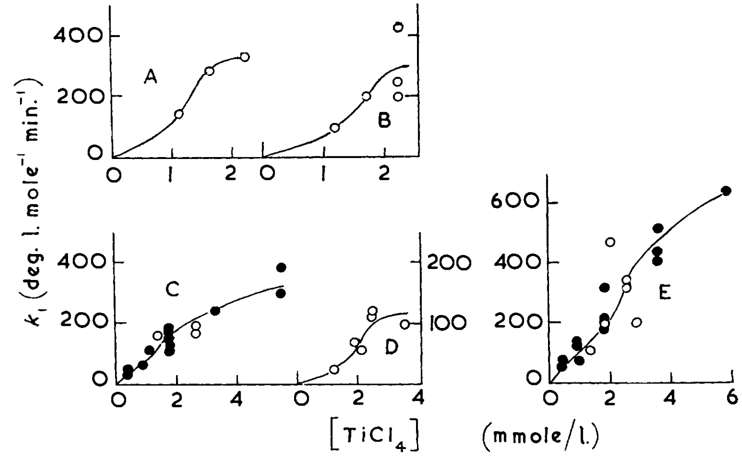

FIG. 5. Variation of k_1 with the concentration of titanium tetrachloride at various temperatures. $[H_2O] > [H_2O]_c$ for all experiments.

Temp.: (A) +5°, (B) −14°, (C) −35°, (D) −61°, (E) −91°.

● Results of P. P. R. ○ Results of R. H. B.

Effect of water concentration. Fig. 7 shows that k_1 becomes independent of the water concentration when this exceeds a certain value which is of the same order of magnitude as, but not identical with, $[H_2O]_C$.

Rate of Reaction at $[H_2O] < [H_2O]_C$.—When the concentration of water was less than $[H_2O]_C$, the polymerisations were incomplete, and the yield, Y, depended on the water concentration in the manner illustrated in Fig. 3.

Between $-60°$ and $-90°$ the order of these reactions ranged from 1·2 to 1·65. Above $-35°$ the order could be determined reliably in only a few experiments and was found to lie between 0·0 and 0·5, approaching zero as the water concentration, and therefore Y, increased.

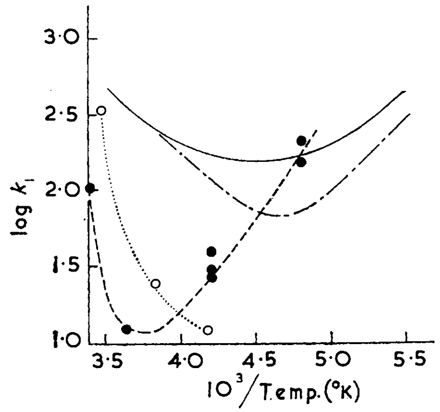

FIG. 6. Variation of k_1 with temperature.

(A) - - — (R. H. B.), [$TiCl_4$] = (1·5—1·7) mmole/l., excess of water.
(B) ——— (P. P. R.), [$TiCl_4$] = (2·0—2·5) mmole/l., excess of water.
(C) ·······○·······○······· (P. P. R.), [$TiCl_4$] = (2·0—2·5) mmole/l., [H_2O] = (0·027—0·030) mmole/l.
(D) — ● – – ● — (P. P. R.), [$TiCl_4$] = (2·0—2·5) mmole/l., [H_2O] = 0·010—0·011) mmole/l.

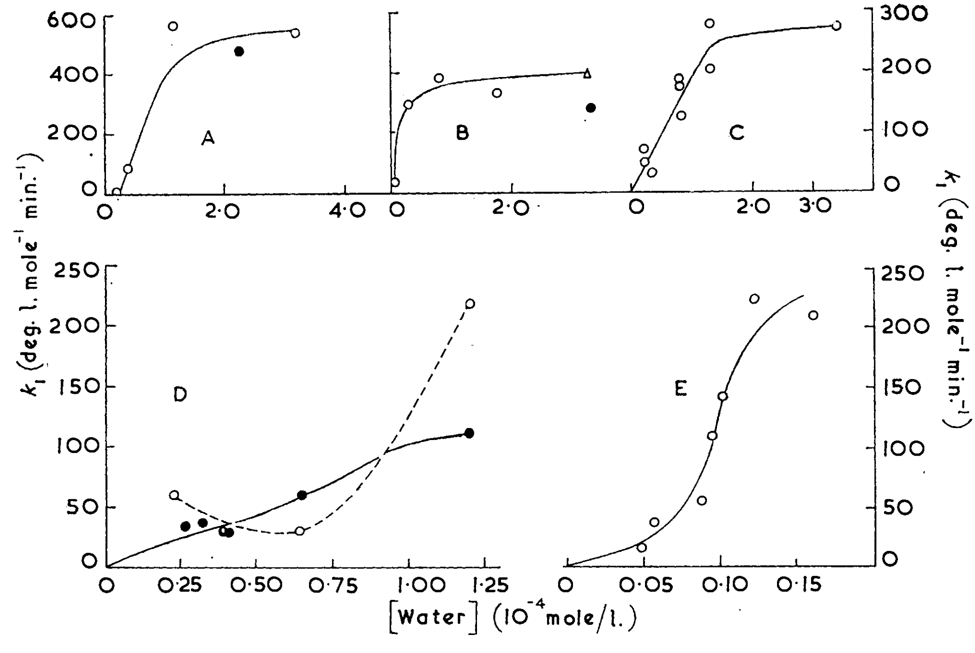

FIG. 7. Variation of k_1 with the concentration of water at various temperatures.

Fig.	Point	Temp.	[$TiCl_4$] (mmole/l.)	Fig.	Point	Temp.	[$TiCl_4$] (mmole/l.)
A	○	+18°	2·10	C		−14°	2·20
* A	●	,,	1·05	D	○	−35	2·54
B	○	+5	2·15	D	●	,,	1·27
† B	△	,,	1·61	E		−61	2·40
* B	●	,,	1·07				

* $k_1 \times 2$. † $k_1 \times 4/3$.

Because of the difficulty of experimentation at extremely low concentrations of water, the variation of the rate with the concentration of monomer and catalyst was not investigated for these conditions.

Fig. 7 also shows that at all temperatures k_1 increases to an asymptotic value. Fig. 7D indicates—in agreement with the results quoted in the previous section—that the limiting value of k_1 is proportional to the concentration of titanium tetrachloride. The variation of the limiting value of k_1 with temperature is shown in Fig. 6.

Effect of Temperature on Rate of Polymerisation.—The effect of the temperature on the rate of polymerisation is shown in terms of its effect on k_1 in Fig. 6. It is evident that the manner in which k_1 varies with temperature depends critically on whether the water concentration is greater or less than $[H_2O]_c$. When the concentration of water exceeds $[H_2O]_c$ (curves A and B), k_1 goes through an extended, flat minimum, so that between about $-35°$ and $-75°$ it is almost independent of temperature. The results obtained with "residual" water, *ca.* 10^{-5} mole/l. (curve D), indicate a sharper minimum near $-5°$; the low-temperature branch of this curve must merge with those of curves A and B, since below about $-75°$ the "residual" water concentration is of the same order of magnitude as $[H_2O]_c$. The points corresponding to a water concentration of $2{\cdot}7 \times 10^{-5}$ mole/l. (curve C) fall between curves B and D, which means that all these results present a self-consistent picture.

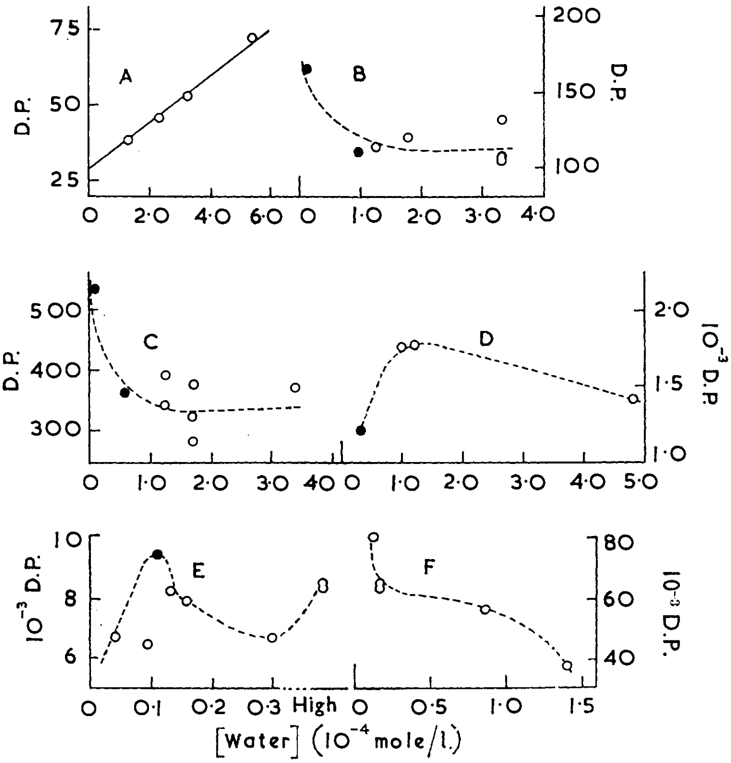

FIG. 8. Effect of concentration of water on the degreee of polymerisation at various temperatures.

Fig.	Temp.	[Isobutene] (mole/l.)	Fig.	Temp.	[Isobutene] (mole/l.)
A	+18°	0·085	D	−35°	0·092
B	+5	0·087	E	−61	0·096
C	−14	0·089	F	−91	0·100

● Reactions were stopped by addition of methanol.

Degree of Polymerisation (D.P.).—The majority of polymerisations which had failed to reach completion because of an insufficiency of water were allowed to reach 100% reaction by the addition of more water, sometimes by admitting moist air to the system. However, in a number of polymerisations in which the concentration of water was insufficient for complete reaction, the catalyst was destroyed by the addition of methanol; the corresponding points are marked specially in Fig. 8. These experiments (two at +5° and at −14°, one each at −35° and at −61°) and others [14] indicate that at these temperatures the D.P. decreases with increasing conversion. On the other hand, at −91° the D.P. is almost independent of monomer concentration and therefore of conversion (see below).

Effect of Water Concentration on D.P.—The effect of water concentration on D.P. is also shown in Fig. 8. It is evident that the critical water concentration $[H_2O]_c$ is probably not a significant quantity in this context, and thus the whole range of water concentrations will be considered together.

The results at 18° are unambiguous, the D.P. increasing rectilinearly with the water concentration.

At all other temperatures the picture appears at first sight rather confused. However, the results are all compatible with the same type of curve, which has a maximum at very low water concentration. This is followed by a plateau, or possibly a shallow minimum, and then a falling branch at the highest water concentrations. The scatter of these results is probably due to the fact that the two turning points of the curve lie at water concentrations which are so close to the residual water level that small variations in this from one experiment to another would have a great effect on the D.P.

Degree of Polymerisation at $[H_2O] > [H_2O]_c$.—Although the critical water concentration has no direct significance for the D.P. it is convenient to consider as a group the results obtained at water concentrations greater than $[H_2O]_c$, because this is equivalent to selecting those experiments in which the polymerisations went to completion without the addition of a second dose of water. The effects of temperature and of the concentrations of titanium tetrachloride and monomer on the D.P. were examined by a series of experiments in most of which the water concentration corresponded to the plateau region of Fig. 8. It was found that generally the D.P. was less reproducible at the lower end than in the upper region of the temperature range, probably because at the lowest temperatures so little water was used that the total water concentration was in fact not in the plateau region, but close to the region where the peak D.P. occurs.

Effect of Monomer Concentration on D.P.—The dependence of the D.P. on the monomer concentration at temperatures down to −48° is shown in the form of Mayo plots in Fig. 9 and at lower temperatures as direct plots in Fig. 10. Some results obtained at very high monomer concentrations by Dr. C. J. Panton are presented in Table 5. In the higher temperature range the Mayo plots are rectilinear. At −61° and below the results are unaccountably erratic. The D.P. increases up to an isobutene concentration of about 0·1 mole/l., and beyond this it appears to be independent of monomer concentration.

TABLE 5.

D.P.'s and yields obtained at −90° with high monomer concentrations.

$[P_1]$ (mole/l.)	1	2	5
Y (%)	6	1·5	0·5
10^3D.P.	73·2	82·2	73·2

In all experiments quoted, $[H_2O] > [H_2O]_c$.

Effect of Concentration of Catalyst.—The D.P. was independent of the concentration of titanium tetrachloride at all temperatures (Table 6).

Variation of D.P. with Temperature.—Fig. 11 shows the manner in which the D.P. varies at three monomer concentrations. At the lowest temperatures the D.P. becomes almost independent of temperature. The slope of the rectilinear part of the curves increases with monomer concentration. The corresponding activation energies, $E_{\text{D.P.}}$, are shown in Table 7.

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[14] Penfold and Plesch, unpublished; Penfold Thesis, Birmingham, 1963.

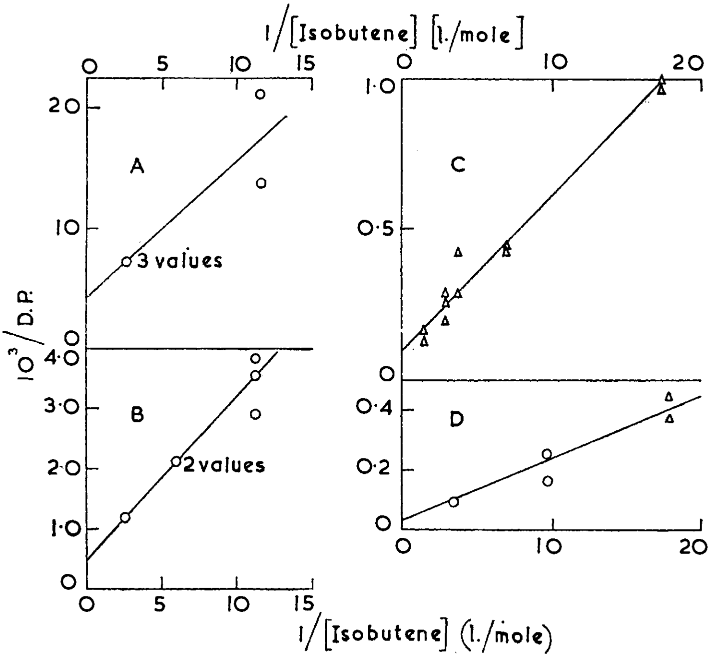


FIG. 9. Variation of 1/D.P. with 1/[Isobutene] from +18° to −48°.
[TiCl$_4$] = (A) 1·05 mmole/l. at +18°; (B) 1·10 mmole/l. at −14°; (C) 0·80 mmole/l. at −35°; (D) (1·49—1·94) mmole/l. at −48°. [△, R. H. B.; ○, P. P. R.]

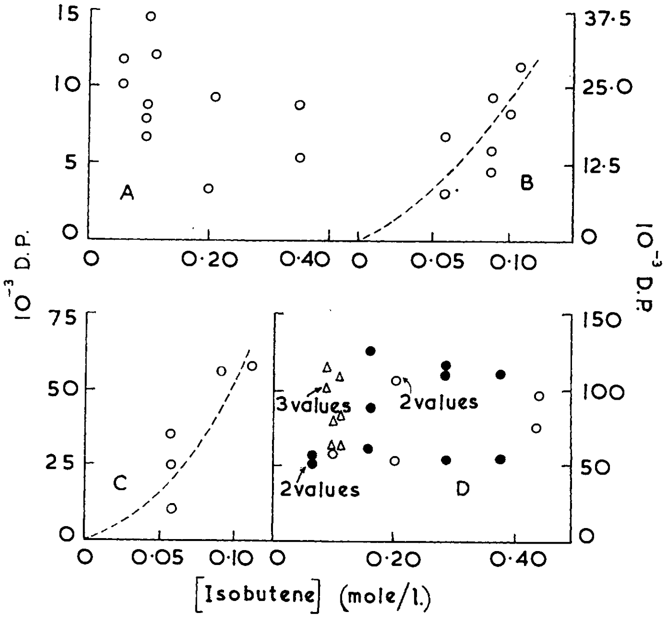


FIG. 10. Dependence of the degree of polymerisation on the concentration of isobutene from −61° to −91°.
(A) $T = -61°$; (B) $T = -72°$; (C) $T = -80°$; [TiCl$_4$] variable in A, B, and C; (D) [TiCl$_4$] = 0·085 (●), 1·24 (○), and (1·75—2·48) (△) mmole/l., $T = -91°$.

TABLE 6.

The effect of [$TiCl_4$] on the D.P. in the presence of an excess of water.

T_i *	Expt. no.	[$TiCl_4$] (mmole/l.)	[Isobutene] (mole/l.)	10^{-3} D.P.
+18°	129	1·05	0·370	0·136
	130	3·16	,,	0·136
+5	97	1·07	0·087	0·107
	98	1·61	,,	0·102
	106	2·15	,,	0·118
−14	101	1·10	0·0893	0·282
	102	1·66	,,	0·321
	107	2·20	,,	0·283
−32	P41	0·32	0·0606	1·06
	P46	0·81	,,	0·995
	P43	0·88	,,	0·975
	P10	1·60	,,	1·09
	P30	1·60	,,	1·10
	P47	1·60	,,	1·11
−37	92	0·46	0·0924	2·25
	54	1·27	,,	1·78
	50	2·55		2·25
−61°	103	1·18	0·0960	8·34
	71	2·37	,,	8·52
	72	2·37	,,	6·77
	74	2·37	,,	7·88
−91	P16	0·35	0·0665	62·2
	P37	0·35	,,	47·9
	P33	0·89	,,	51·0
	P38	0·89	,,	55·6
	P59	0·89	,,	50·6
	P8	1·76	,,	51·3
	P53	1·76	,,	75·0
	P12	3·52	,,	47·5
	P35	3·52	,,	64·3
	P52	3·52	,,	78·2
−91	110	1·24	0·100	57·0
	10	2·05	,,	83·4
	76	2·48	,,	79·7
	77	2·48	,,	64·2
	40	2·77	,,	63·3

* See footnote to Table 1.

TABLE 7.

The " activation energy " of the D.P.

[Isobutene] (mmole/l.)	400	97	56
$E_{D.P.}$ (kcal./mole)	−8·6	−8·2	−6·6

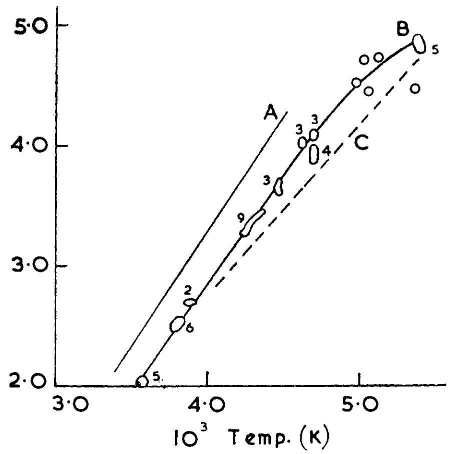


FIG. 11. Variation of the D.P. with temperature (°K).

[Isobutene] = (A) 400, (B) 97, (C) 56 mmole/l. Experimental points are shown only for curve B. The numbers indicate the number of results enclosed by the adjacent area.

GENERAL DISCUSSION

For convenience the facts established by our results are summarised here, together with the more obvious conclusions arising from them.

Yield.—(1) The increase of Y with the water concentration to $Y = 100\%$ at $[H_2O]_c$ means that : (*a*) water (or another co-catalyst) is necessary for the reaction; (*b*) water is consumed during the reaction; (*c*) this consumption of water is a kinetic chain-termination.

(2) From +18° to −35° $[H_2O]_c$ decreases by a factor of two, and from −35° to −61° by a factor of seven (Table 2). An Arrhenius-type plot of these results is strongly curved and suggests a change in reaction mechanism at temperatures below −35°.

The Degree of Polymerisation.—(3) Extrapolation of curve B of Fig. 11 to log D.P. = 0 gives an upper limit of about 140° for the ceiling temperature of polyisobutene for a concentration of 0·1 mole/l.

(4) The change of slope of curve B in Fig. 11 at low temperatures is similar to that found by Kennedy and Thomas [15] for the polymerisation of isobutene by aluminium trichloride.

(5) The variation of the slope of the linear part of the log D.P.–$1/T$ plots with monomer concentration, although small, is in the opposite direction to that reported by Kennedy and Thomas.[15]

(6) A detailed interpretation of the variation of D.P. with temperature requires a knowledge of the factors affecting the D.P. and of the temperature coefficients of the relevant chain-breaking coefficients. These points are discussed below.

(7) Since the D.P. is independent of the concentration of titanium tetrachloride, this compound itself cannot be involved in any chain-breaking reaction, nor can any reaction product whose concentration is governed by that of the titanium tetrachloride.

(8) Most of the D.P.'s recorded in this Paper are those of polymers obtained at high or complete conversion, and therefore two points must be considered before chain-breaking coefficients can be evaluated from the Mayo plots. Litt's criticism [16] that the variation in the relation between the number-average and viscosity-average D.P.'s with conversion must be taken into account, is not seriously relevant here, since it has been shown that the constants in the Mark–Houwink equation relating D.P. to $[\eta]$ are almost the same for whole and for fractionated polyisobutenes,[17] and are therefore unlikely to change much with conversion.

The second point concerns the variation of D.P. with conversion. Instead of adopting the procedure recommended by Higashimura, Okamura, and Sakurada [18] we have assumed that 1/D.P. is proportional to $2/[\mathrm{P}_1]_0$ for our calculations, *i.e.*, we made the simplifying assumption that the whole polymerisation took place at a constant monomer concentration equal to half the initial monomer concentration. The great speed of the reactions made it impossible to stop them at low conversion, and this approximation, though not strictly valid, will give better values of the chain-breaking coefficients than a correlation of D.P. with $[\mathrm{P}_1]_0$. We thank a referee for pointing out that errors arising from the use of D.P.'s at high conversion increase with conversion, and that some of the scatter of our D.P. results may have been due to this effect.

(9) The detailed interpretation of the results requires that the kinetics of the propagation reaction be elucidated, for it is not possible to say *a priori* whether this is bimolecular, as is usually assumed, or unimolecular, as in the cationic polymerisation of propene [3] and that of isobutene at high monomer concentrations.[19] The variation of the D.P. with monomer concentration provides one of the clues. The argument is this:

Let the rate of chain propagation be given by the equation

$$V_2 = k_2[\mathrm{P}_n^+][\mathrm{P}_1]^x \qquad (2)$$

where x may be 0 or 1. Consider also a chain-breaking reaction involving the monomer, the rate of which is given by the equation

$$V_3 = k_3[\mathrm{P}_n^+][\mathrm{P}_1] \qquad (3)$$

Let the total rate of chain-breaking be given by

$$V_\mathrm{b} = V_3 + J[\mathrm{P}_n^+] \qquad (4)$$

where J includes all termination and transfer reactions hitherto unspecified. Then the D.P. is given by

$$k_2/\mathrm{D.P.} = 2^{1-x}k_3[\mathrm{P}_1]_0^{1-x} + 2^xJ/[\mathrm{P}_1]_0^x \qquad (5)$$

[15] Kennedy and Thomas, *J. Polymer Sci.*, 1961, **55**, 311.
[16] Litt, *J. Polymer Sci.*, 1960, **43**, 567.
[17] Thomas, *Trans. Faraday Soc.*, 1961, **57**, 511.
[18] Higashimura, Okamura, and Sakurada, *J. Polymer Sci.*, 1958, **33**, 496.
[19] Kennedy, Kirshenbaum, Thomas, and Murray, *J. Polymer Sci.*, 1963, *A*1, 331.

The results show that, down to at least —48°, 1/D.P. is rectilinearly related to $1/[P_1]_0$, which means that $x = 1$, and therefore

$$1/\text{D.P.} = k_3/k_2 + 2J/k_2[P_1]_0 \qquad (6)$$

This means that between +18° and —48° the propagation reaction is of first order with respect to the monomer concentration, an extremely important conclusion because it disposes of the need to consider a Fontana–Kidder type of propagation reaction, which is of zero order with respect to monomer concentration.[3]

The D.P. results obtained at temperatures below —48° are unfortunately so scattered that their significance is obscure. However, it is just in this temperature region that the rate curves are of first order and this makes the Fontana–Kidder type of propagation very unlikely.

(10) The chain-breaking process characterised by the rate constant k_3 is regarded as a monomer transfer, *i.e.*, proton transfer from growing chain to monomer. The values of k_3/k_2 derived from the Mayo plots are presented in the form of an Arrhenius plot in Fig. 12. The results in Table 5, together with those of Fig. 10D show that at —90° the D.P. is almost independent of $[P_1]$ when this exceeds *ca.* 0·1 mole/l. This indicates that the D.P. is controlled essentially by k_3/k_2, and the corresponding value of this is included in Fig. 12.

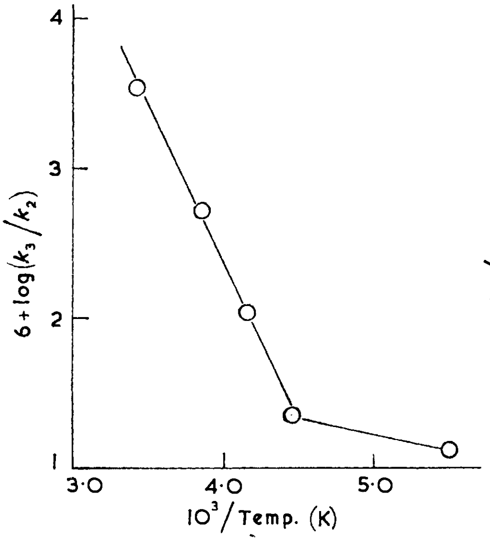


FIG. 12.

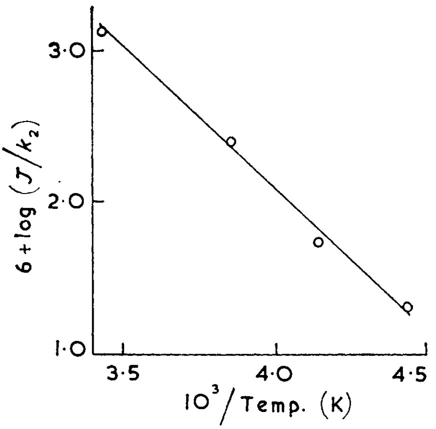


FIG. 13.

FIG. 12. Variation of k_3/k_2 with temperature.
FIG. 13. Variation of J/k_2 with temperature.

(11) The slope, S, of the monomer Mayo plot is given according to equation (6) as

$$S = 2J/k_2 \qquad (7)$$

The temperature-dependence of J/k_2, is shown in Fig. 13. The chain-breaking reactions which are included in J will be discussed below.

The D.P. results in Figs. 10A—D are so scattered that values of J/k_2 cannot be derived from them. We ascribe the scatter to the effects of small changes in the water concentration and of impurities becoming more important the lower the temperature.

In the earlier publication [6] values of k_m/k_p (corresponding to the present k_3/k_2) at —60° and —75°, and of $(k_t + J)/k_p$ (corresponding to the present J/k_p) at —60° were given, which were derived before the complete results considered here were available. They cannot now be considered valid.

(12) The significance of the D.P.'s obtained with water concentrations less than $[H_2O]_c$ is obscured by the variation of D.P. with conversion, and moreover most of these reactions were allowed to go to completion by the addition of a second dose of water. Therefore only experiments conducted with $[H_2O] > [H_2O]_c$, *i.e.*, those in which the polymerisation had gone to completion, can give useful information on the role of water as chain-breaking agent. For this reason also the maxima in the D.P. plots are not amendable to analysis by Plesch's theory.[20a]

The results show that at $+5°$ and $-14°$ the D.P. is almost independent of $[H_2O]$ when this exceeds $[H_2O]_c$. Mayo plots of the results obtained at -35, -61, and $-91°$ suggest that 1/D.P. increases rectilinearly with $[H_2O]$ when this exceeds $[H_2O]_c$. This indicates that there is a chain-breaking species, the concentration of which is proportional to $[H_2O]$. If the concentration of this species is assumed to be equal to $[H_2O]$, the following values of k_w/k_2, defined by

$$k_w/k_2 = [P_1]_0\Delta(1/\text{D.P.})/2\Delta[H_2O]$$

can be derived:

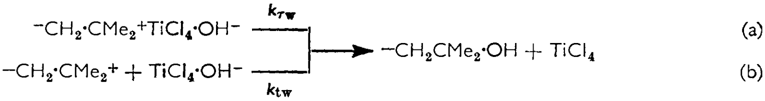
Temp.	$-35°$	$-61°$	$-91°$
k_w/k_2	8·7	3	0·3

Since, however, the concentration of the species involved may well be smaller than $[H_2O]$, these are minimum values, and they show that the chain-breaker concerned is by far the most efficient one in the system. Since the values of k_w/k_2 are rather uncertain and since, moreover, the relation between $[H_2O]$ and the concentration of the chain-breaker may change with temperature, the calculation of a value for $E_w - E_p$ is not justified. The above figures and argument supersede the preliminary data presented in Table 6 of ref. 6.

The End-groups.—(13) The infrared spectra of the polyisobutenes of low D.P.—either whole polymers prepared at relatively high temperatures or the early fractions obtained from the fractionation of higher polymers [13]—show absorption bands indicating the presence of hydroxyl groups. Such groups, which could hardly be other than terminal, could be formed by various transfer or termination reactions which will be considered in detail.

The evidence discussed in sections (1) and (12), and the fact that the kinetic order of the polymerisations is higher when $[H_2O] < [H_2O]_c$ than when $[H_2O] > [H_2O]_c$, show that there is at least one termination reaction, the rate of which depends on the concentration of a species which is determined by that of the water. Depending upon the conditions, this reaction, represented by equation (i), may be unimolecular or bimolecular, or both orders may occur concurrently.

(i)

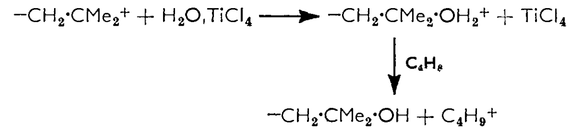


$$\begin{tikzcd}
{-CH_2\cdot CMe_2{}^+TiCl_4\cdot OH^-} \arrow[dr, "k_{Tw}"] & & (a) \\
& {-CH_2CMe_2\cdot OH + TiCl_4} & \\
{-CH_2\cdot CMe_2{}^+ + TiCl_4\cdot OH^-} \arrow[ur, "k_{tw}"'] & & (b)
\end{tikzcd}$$

The rates of both processes will be included in J.

The only transfer reaction which would yield a terminal hydroxyl group is the following:

(ii)



$$\begin{tikzcd}
{-CH_2\cdot CMe_2{}^+ + H_2O,TiCl_4} \arrow[r] & {-CH_2\cdot CMe_2\cdot OH_2{}^+ + TiCl_4} \arrow[d, "C_4H_8"] \\
& {-CH_2\cdot CMe_2\cdot OH + C_4H_9{}^+}
\end{tikzcd}$$

Some of the hydroxyl groups could also have been formed when the reactions were " killed " by admission of moist air or addition of methanol.

(14) The double bonds in the polymer could arise from proton transfer to monomer, discussed in section (10), or from proton transfer to the anion. In view of the conclusions

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[20] Plesch, (*a*) *J.*, 1964, 104; (*b*) *Z. Elektrochem.*, 1956, **60**, 325.

in section (1, *b* and *c*) this reaction, which is a catalyst regeneration,[20b] cannot be important in this system, and therefore the unsaturation must be principally due to monomer transfer.

(15) The chlorine in the polymers, revealed by elementary analysis, could arise from three sources:

(*a*) Abstraction of a chloride ion from titanium tetrachloride. This reaction need not be considered, since the D.P. is completely independent of the concentration of titanium tetrachloride.

(*b*) A termination reaction similar to reaction (i), in which a chloride ion instead of a hydroxyl ion effects the neutralisation:

$$\text{(iii)} \qquad -CH_2\cdot CMe_2{}^+TiCl_4\cdot OH^- \xrightarrow{k_{\tau h}} -CH_2\cdot CMe_2Cl + TiCl_3\cdot OH$$

This unimolecular reaction is kinetically indistinguishable from reaction (i-a), and any kinetic estimates of the rate constant for unimolecular termination will give $k_\tau = k_{\tau w} + k_{\tau h}$. Just as we considered a bimolecular analogue (i-b) of reaction (i-a), so we need to consider a bimolecular variant of reaction (iii), the rate constant of which will be denoted by k_{th}. Both $k_{\tau h}$ and k_{th} will be included in J.

(*c*) Solvent transfer according to reaction (iv):

$$\text{(iv)} \qquad -CH_2\cdot CMe_2{}^+ + CH_2Cl_2 \xrightarrow{C_4H_8} -CH_2\cdot CMe_2Cl + Cl\cdot[CH_2]_2\cdot CMe_2{}^+$$

Each transfer reaction of this kind gives a pair of molecules containing terminal chlorine atoms. The rate-constant of this chain-breaking reaction will also be included in J.

(16) On the basis of the foregoing discussion we could now formulate the complete Mayo equation governing the D.P. of the polymers. But in order to do this rigorously, *it is necessary to distinguish clearly at this stage the reactions of free ions and those of ion-pairs.* Up to the present no explicit assumption has been made about the nature of the propagating species, and it has been assumed implicitly that there is only one such species. It will be shown below, in the section on kinetics and mechanism, that simultaneous propagation by free ions and ion-pairs is a useful theory, and some of the relevant equations, including the Mayo equation, will be derived there.

The Rate of Reaction.—(17) At $[H_2O] > [H_2O]_c$ the initial rate depends on the first power of the initial monomer concentration, *i.e.*, the external order of the reactions is unity, both at −91° and at −31°. However, at −31° and higher temperatures the internal order over the major part of the reactions is zero. The change of internal kinetic order suggests that the nature of the rate-controlling process(es) changes with temperature.

(18) The first-order rate constant, k_1, defined by equation (1) increases with the titanium-tetrachloride concentration at all temperatures in a manner which can be interpreted by an S-shaped curve. These curves are similar to that obtained previously for the polymerisation of isobutene by titanium tetrachloride in hexane.[21] The evidence suggests that the concentration of the growing chains is governed by at least one equilibrium.

(19) At all temperatures the variation of k_1 with the water concentration follows an S-shaped curve to a maximum limiting value, which agrees closely with that obtained from the variation of the titanium-tetrachloride concentration. The similarity in the shapes of the curves relating k_1 to the concentrations of water and of titanium tetrachloride suggests a reciprocity arising from at least one equilibrium governing the reaction rate.

(20) The water concentration at which k_1 becomes independent of $[H_2O]$ is smaller than the titanium-tetrachloride concentration by a factor of 5—20 between +18° and −35°, and a factor of about 150 at −61°. This must mean that either the greater part of the titanium tetrachloride is unavailable, perhaps because of complex formation with the monomer,[22] or that equilibrium formation of a multiple complex, *e.g.*, $3TiCl_4,2H_2O$, is involved.

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[21] Plesch, *J.*, 1950, 543.

[22] Longworth, Plesch, and Rutherford, "International Conference on Co-ordination Chemistry," Chem. Soc. Special Publn. No. 13, p. 115.

(21) The variation of k_1 with temperature is without parallel in the literature of cationic polymerisation and presents the greatest obstacle to an interpretation of the reaction. It indicates clearly that the relative importance of two (or more) rate-determining processes must change with the temperature, and that the onset of this change is determined by the concentrations of water and catalyst.

KINETICS AND MECHANISM

One of the most striking features emerging from our results is that the behaviour pattern of the polymerisation is very different at the two ends of the temperature range. The most important instances of this are summarised below.

(*a*) The reproducibility is much better above about $-50°$ than below this temperature.

(*b*) The internal order of the reactions goes from zero at high temperatures to unity at the lowest temperatures, if the quantity of water present is sufficient to give a yield of 100%.

(*c*) The rate constant, k_1, passes through a minimum.

The explanation of (*c*), we thought, might lie in a dielectric acceleration. Over the temperature range concerned, the dielectric constant of methylene dichloride increases [9] from about 8 to about 15, and since the rate of many ionogenic reactions increases with the dielectric constant of the solvent, it seemed possible that the initiation reaction is dielectrically accelerated to an extent adequate to overcome the thermal deceleration, and the termination correspondingly retarded. Beard and Plesch [23a] have, however, shown that for a Menschutkin reaction (in methylene dichloride) which is closely analogous to the initiation reaction, there is no dielectric acceleration, the Arrhenius plot being strictly rectilinear between $+30°$ and $-71°$.

It follows that we must seek the origin of the phenomena in the propagation reaction. We therefore propound the hypothesis that in these systems there are two types of propagating species, namely, free ions and ion-pairs, which have different kinetic characteristics, and whose relative concentrations are governed by a mobile equilibrium. From the inception of the idea of ionic polymerisation it should have been obvious that since in all relevant systems both types of ions must exist, the simultaneous occurrence of two types of growth processes and chain-breaking processes was to be expected. The analogous problem in small-molecule kinetics has received some attention,[24] but in regard to cationic polymerisations this aspect has been largely neglected.

Polymerisations in which the reaction is propagated by more than one type of active end will be termed enieidic; * evidently polymerisations in which both free ions and ion-pairs propagate the reaction represent one class of enieidic polymerisation. The relevant parts of the theory of these reactions will be elaborated below; other aspects will be discussed elsewhere.

For simplicity, concentrations will be denoted by lower-case letters: m for monomer concentration, p for concentration of growing chains which are free, q for that of ion-pairs in which the cation is a growing chain. The rate constants for the reactions of free ions will be denoted by Latin subscripts, those for the reaction of ion-pairs by Greek subscripts. We assume that all rate and equilibrium constants are independent of chain-length.

The Dissociation Constant.—The dissociation constant, K, of an ion-pair at temperature

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* From Greek *enioi* = several, *eidos* = form. The purpose of creating this word is to avoid the use of the overworked term " polymorphic." The words monoeidic and dieidic will also be found useful.

[23] Beard and Plesch, (*a*) *J.*, 1964, 3682; (*b*) *J.*, 1964, 4879.

[24] (*a*) Hughes, Ingold, Mok, Patai, and Pocker, *J.*, 1957, 1265; Ross, Finkelstein, and Petersen, *J. Amer. Chem. Soc.*, 1961, **83**, 4853; Zandstra and Weissman, *ibid.*, 1962, **84**, 4408; Monk, " Electrolytic Dissociation," Academic Press, London, 1961; Lichtin and Rao, *J. Amer. Chem. Soc.*, 1961, **83**, 2417; (*b*) Dubois and Barthel, in " International Electrolyte Symposium," ed. Pesce, Pergamon Press, London, 1962, p. 343.

T in a solvent of dielectric constant D is given reasonably accurately by the Bjerrum–Fuoss equation

$$-\log K = A - B/aDT \tag{8}$$

The terms A and B involve only fundamental constants, except that A also involves $\log a$, where a is a quantity, the significance of which has been much discussed, but which is related to, if not equal to, the interionic distance in the ion-pair.[25]

The dissociation constant of the ion-pair $H(C_4H_8)_nCMe_2{}^+TiCl_4{\cdot}OH^-$ can be estimated by taking the radius of the cation as equal to that of the t-butyl ion, 2·8 Å, and the radius of the anion as 4·2 Å; thus $a = 7$ Å. With this value for a and the appropriate values for DT, equation (8) gives $K = 1{\cdot}8 \times 10^{-4}$ mole/l. at 0° and $3{\cdot}3 \times 10^{-4}$ mole/l. at −95°.

The concentration of free ions, p, and of ion-pairs, q, is related to the total concentration of cations, c, by the equations

$$c = p + q \qquad \text{and} \qquad K = p^2/q \tag{9 (a) and (b)}$$

if no ions other than those concerned in the polymerisation are present. Thus, p is given in terms of K and c, if activity coefficients are neglected, by the equation

$$p = -K/2 + (K^2 + 4Kc)^{\frac{1}{2}}/2 \tag{10}$$

The degree of dissociation, α, is p/c. In the systems under consideration the total concentration of cations, c, is very unlikely to be greater than the water concentration, which in typical experiments at the higher temperatures is of the order of 10^{-4} mole/l. For $K = 1{\cdot}8 \times 10^{-4}$ and $c = 10^{-4}$, $\alpha = 0{\cdot}72$. Since c may actually be much less than $[H_2O]$, this is a minimum value of α. At −95° the maximum effective amount of water is of the order of 10^{-5} mole/l.; if we take this value for c, we find $\alpha = 0{\cdot}97$, which also is a minimum value. Thus the degree of dissociation of the ion-pairs in our system increases very considerably as the temperature falls; this is most effectively shown by the ratio of the concentrations of free cations to that of ion-pairs, p/q: this increases from 2·6 at 0° to 32 at −95°.

Whilst the values of K and α, based on the estimated value of a, are probably no more than a useful indication of orders of magnitude, their increases with falling temperature, upon which the present argument is essentially based, are documented beyond dispute, especially for methylene dichloride solutions over the relevant temperature range.[23b]

The Rate of Reaction.—The rate of polymerisation is now given by equation (11):

$$V_2 = (k_p p + k_\pi q)m \tag{11}$$

so that

$$k_1 = V_2/m = k_p p + k_\pi q \tag{12}$$

Evidently the usual logarithmic differentiation with respect to temperature is of little use, and thus the effect of temperature on k_1 must be found by simple differentiation.

Since $\mathrm{d}p/\mathrm{d}T = -\mathrm{d}q/\mathrm{d}T$, if c is constant,

$$\frac{\mathrm{d}k_1}{\mathrm{d}T} = (k_p - k_\pi)\frac{\mathrm{d}p}{\mathrm{d}T} + p\frac{\mathrm{d}k_p}{\mathrm{d}T} + q\frac{\mathrm{d}k_\pi}{\mathrm{d}T} \tag{13}$$

We make the not implausible assumptions that at least over the lower part of the temperature range $k_\pi < k_p$ and $E_\pi > E_p$; then, since $\mathrm{d}p/\mathrm{d}T$ is negative and both $\mathrm{d}k_p/\mathrm{d}T$ and $\mathrm{d}k_\pi/\mathrm{d}T$ are positive, we have an equation which can give a minimum for k_1. Because of the awkward form of the equation its further analytical study is not profitable. However, since p and q are functions of c, it has the implication that the position of the minimum will depend on c, and therefore most probably on the concentration of water and titanium tetrachloride, as the results in Fig. 6 require.

[25] Kay, ref. 24(*b*), p. 119; Sadek, Hirsch, and Fuoss, *ibid.*, p. 132.

Qualitatively the minimum in the rate–temperature curves is explained thus: We assume that to any water concentration less than that corresponding to the turn-over point of the curves in Fig. 7 there corresponds a definite value of the concentration of the catalytic species. To any value of this there corresponds a concentration, c (not necessarily stationary), of growing chains which will increase with decrease in temperature, if the termination has a positive activation energy. Thus, as the temperature is reduced, the decelerating effect through a relatively large E_π is overcome, and the temperature coefficient of k_1 becomes negative because: (*a*) the absolute number of growing chains increases; (*b*) the ratio of free ions to ion-pairs (p/q) increases through the negative temperature coefficient of K; and (*c*) E_p is relatively small.

This qualitative argument, based as it is on a number of somewhat arbitrary assumptions, is less satisfactory than a full analytical treatment of the problem would be. Regrettably, the complexity of our system makes this impossible. However, our theory will be shown to account not only for most of our observations, but also for some hitherto unexplained results of other authors.

The Degree of Polymerisation.—Our aim is to deduce the equation for the D.P., *i.e.*, the Mayo equation, for enieidic polymerisation by free ions and ion-pairs. The rate of propagation is given by equation (11). The rate of unimolecular termination is

$$V_4 = k_\tau q \qquad (14)$$

It is assumed that only ion-pairs can undergo this type of reaction, the chemistry of which is given by reaction (i) or (iii), or both. The rate of bimolecular termination by free anions is

$$V_5 = (k_t p + k_{\tau 2} q)p \qquad (15)$$

where $k_t = k_{tw} + k_{th}$ [see sections (13) and (15) above], if the concentration of anions is equal to p, that of the free, reaction-carrying cations. The rate-constant, $k_{\tau 2}$, characterises the reaction of ion-pairs with free anions. Monomer transfer has a rate given by

$$V_3 = (k_m p + k_\mu q)m \qquad (16)$$

Unspecified chain-breaking reactions are represented by the equation

$$V_6 = J_p p + J_q q \qquad (17)$$

The principal component of the J's is probably the solvent-transfer reaction.

Thus the total rate of chain-breaking is

$$V_b = V_3 + V_4 + V_5 + V_6 \qquad (18)$$

From a combination of equations (11) and (14) through (18) we obtain the Mayo equation in the form

$$\begin{aligned} 1/\text{D.P.} &= V_b/V_2 \\ &= (k_m p + k_\mu q)/(k_p p + k_\pi q) \\ &\quad + q(k_{\tau 2} p + k_\tau + J_q)/(k_p p + k_\pi q)m \\ &\quad + p(k_t p + J_p)/(k_p p + k_\pi q)m \end{aligned} \qquad (19)$$

When equation (19) is compared with the Mayo equation for monoeidic polymerisation two features stand out: the first term, which is independent of monomer concentration and was previously denoted by k_3/k_2, is composite, and so is the coefficient of m in the other terms; and all terms depend weakly on the concentration of growing chains. The composite nature of the terms representing the intercept and slope of the monomer Mayo plots gives at least a qualitative explanation for the non-linearity of the corresponding Arrhenius plots. With regard to the intercept, the first term of equation (19), this aspect can be elaborated as follows:

If at the higher temperatures $k_\mu q$ is appreciably greater than $k_m p$, and $k_\pi q$ greater than $k_p p$, and if the reverse is true at the lower temperatures, then the " activation energy " of 10 kcal./mole corresponding to the high-temperature branch of the Arrhenius plot of k_3/k_2 is, at least approximately, equal to $E_\mu - E_\pi$, and the " activation energy " of 1·5 kcal./mole corresponding to the low-temperature branch of the plot approximates to $E_m - E_p$. The assumption, which has been made above, that the activation energy for propagation is smaller for the free cation than for one which is associated with an anion ($E_p < E_\pi$), seems reasonable, because in the latter case a charge which is initially more diffuse than in the free ion needs to be concentrated in the transition state. If this assumption is valid, it follows that $E_\mu < E_m$, which means that the activation energy for transferring a proton to the monomer from a free cation is greater than that for proton transfer from a paired cation; and this too seems intelligible in terms of differences in charge density.

The bend in the Arrhenius plot of the D.P. reflects the change in the temperature coefficients of k_3/k_2 (Fig. 12) and therefore the temperature at which the reaction pattern begins to be dominated by the free cations. Moreover, since the free cations are probably much more reactive than the paired cations, the greater scatter of our results at the lower temperatures can reasonably be attributed to a greater effectiveness of water and impurities as chain-breakers.

Considering now the slope, S, of the Mayo monomer plot, which is the coefficient of $1/m$ in equation (19), it is evident that since this contains (at least) five terms in the numerator no useful information can be obtained from it or from its variation with temperature at this stage.

Comparison with the Results of Other Workers.—The theory of enieidic polymerisation by free ions and ion-pairs has implications which can be tested by comparison with results available in the literature. Since the dissociation constant of the ion-pairs diminishes rapidly as the sum of the radii of the ions decreases [see equation (8)], the temperature at which the participation of the free ions becomes dominant should decrease likewise. It will be recalled that the change in the temperature coefficient of the intercept of the Mayo monomer plots which is reflected in the change of slope of the log D.P.–$1/T$ plots, was attributed to the coming into prominence of propagation by free ions. Thus the existence and location of such a bend in the log D.P.–$1/T$ plot characterises this feature. In agreement with our theory the results of Kennedy and Thomas [15] on the polymerisation of isobutene by aluminium chloride show that for solutions in ethyl chloride and vinyl chloride the temperature at which the plot of log D.P. against $1/T$ bends over to become almost horizontal lies in the region $-80°$ to $-90°$, whereas for our experiments with titanium tetrachloride it is about $-70°$. We ascribe this to the fact that the radius of $TiCl_4X^-$ ion is about 4·2 Å, whereas that of an $AlCl_3X^-$ ion is about 3·8 Å ($X = Cl$ or OH). Furthermore, the corresponding plot for catalysis by boron fluoride [26] shows no such turning point down to $-105°$, showing that down to this temperature the contribution of free ions to the reaction is negligible; the radius of the BF_3X^- ion is about 2·8 Å. Conversely, the polymerisation of isobutene in ethyl chloride by stannic chloride at $-78°$ has been shown to be most easily interpreted in terms of a dominant propagation by free ions, which is intelligible in terms of the probably six-fold co-ordinated, and therefore much greater, anion.[6,27]

A further consequence of the theory is that since the dissociation constant of ion-pairs falls rapidly as the dielectric constant of the solvent decreases, the temperature at which the contribution of the free ions to the reaction becomes important should decrease with the polarity of the solvent. This is borne out by the results of Kennedy and Thomas,[15] which show that for the polymerisation of undiluted isobutene the plot of log D.P. against

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[26] Results of Thomas *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 276, recalculated by Flory, " Principles of Polymer Chemistry," Cornell University Press, Ithaca, N.Y., p. 218.

[27] Norrish and Russell, *Trans. Faraday Soc.*, 1952, **48**, 91.

$1/T$ does not depart from linearity down to $-98°$, and that in polar solvents the higher the monomer concentration the lower is the temperature at which the curve bends over. However, experiments by the same workers[28] conducted in propane solution down to $-145°$ showed that the log D.P.–$1/T$ plot does bend over at about $-105°$. Since for hydrocarbons, in contrast to polar solvents, the product D.T. decreases as T decreases, this phenomenon cannot be explained as previously. Most probably it is ascribable to enhancement of dissociation by increased solvation of free ions by the small quantities of ethyl chloride added as vehicle for the catalyst. It is also likely that, at these very low temperatures, solvation of the ions by the monomer will have some effect.

We thank Polymer Corporation of Canada for a research studentship (R. H. B.) and a post-doctoral fellowship (P. P. R.), and for the gift of apparatus and materials, and Shell Research Ltd., for the chlorine analyses and gifts of di-isobutene.

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[*Received, March 6th*, 1964.]

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[28] Kennedy and Thomas, *Adv. Chem.*, 1962, **34**, 111.