

**492. The Low-temperature Polymerisation of Isobutene. Part V.¹
Polymerisation by Aluminium Trichloride in Methylene Dichloride.**

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Qualitative and kinetic experiments between 0 and -60° have shown that the polymerisation of isobutene by aluminium trichloride in methylene dichloride does not require water as a co-catalyst, and that water does not affect the rate but does reduce the yield of precipitable high polymer and its molecular weight. Co-catalysis by the solvent is thought to be the most probable explanation. The rate of polymerisation decreases and the molecular weight of the polymer increases with fall in temperature.

THERE is much evidence² that many metal halides will not polymerise isobutene unless an ionogenic substance, the co-catalyst, is present. However, there is no rigorous proof that aluminium trichloride requires a co-catalyst to polymerise isobutene, although Jordan and Treloar³ showed that it does in order to polymerise undiluted styrene. We set out to resolve this question and to obtain measurements of the rate of polymerisation, since it had been alleged that, when catalysed by aluminium trichloride, the reaction is too fast to be followed.⁴ The principal difficulty is the very low solubility of aluminium trichloride in methylene dichloride (and, indeed, in all solvents of interest to us).

EXPERIMENTAL

Materials.—Isobutene was purified as previously described.^{4,5} The dosing bulbs of the polymerisation apparatus⁵ were replaced by a burette, thermostated at 0° , with which the volumes of liquid isobutene could be measured to ± 0.025 ml. Phials containing measured volumes of thoroughly dried isobutene (various amounts) and methylene dichloride (0.8 ml.) were prepared by distilling the components from burettes *in vacuo*. Methylene dichloride was purified⁶ and dosed⁵ as described previously. Aluminium trichloride was prepared by a method similar to that of Wallace and Willard;⁷ it was sublimed into small glass phials, and the weight of the contents was determined by the mid-point method.⁸

Apparatus and Method.—The polymerisations were carried out in an adiabatic calorimeter.⁵ The progress of polymerisation was recorded on a Sefram "Graphispot" recording galvanometer which registered the out-of-balance current in the Wheatstone bridge circuit.

The water content of the reaction mixtures was varied by varying the time (t_p) for which the apparatus was evacuated before being charged with the reagents: in some experiments it was reduced to the lowest value obtainable by flushing the system with trimethylchlorosilane vapour.

The polymers were isolated from the mixtures by precipitation in ethanol, and their molecular weights obtained by viscometry of solutions in di-isobutene.

RESULTS

The work consists of a group of qualitative experiments to determine whether the polymerisation requires the presence of water, and a set of quantitative experiments involving rate, yield, and molecular weight measurements.

Qualitative Experiments.—The qualitative experiments were carried out between -2 and $+4^{\circ}$, with an isobutene concentration of 116 ± 12 mmoles/l. The reactions were started by breaking the phial containing solid aluminium trichloride into the monomer solution. The

¹ Part IV, Biddulph and Plesch, *J.*, 1960, 3913.² "The Chemistry of Cationic Polymerisation," ed. Plesch, Pergamon Press, Oxford, 1963.³ Jordan and Treloar, *J.*, 1961, 737.⁴ Kennedy and Thomas, *J. Polymer Sci.*, 1960, **46**, 481; 1961, **55**, 311; *Adv. Chem.*, 1962, **34**, 111; Kennedy, Kirshenbaum, and Thomas, *J. Polymer Sci.*, 1963, **A,1**, 331.⁵ Biddulph and Plesch, *Chem. and Ind.*, 1959, 1482.⁶ Longworth, Plesch, and Rigbi, *J.*, 1958, 451.⁷ Wallace and Willard, *J. Amer. Chem. Soc.*, 1950, **72**, 5275.⁸ Rutherford, *Chem. and Ind.*, 1962, 1614.

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most obvious feature was the variation in the shape of the reaction curves; they became more S-shaped as the pumping time was decreased. Since the rate of solution of the catalyst may have affected the reaction, neither the nominal catalyst concentration nor the rate of reaction are

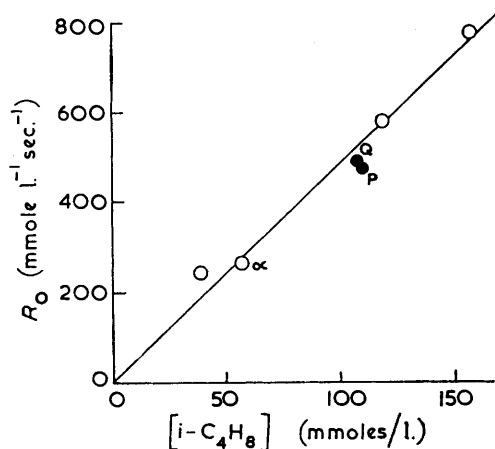


FIG. 1. The variation of R_0 with isobutene concentration at -35° .

○, $[\text{AlCl}_3] = 1.43 \pm 0.07$ mmoles/l. P, $[\text{AlCl}_3] = 0.57$ mmole/l. Q, $[\text{AlCl}_3] = 0.87$ mmole/l.

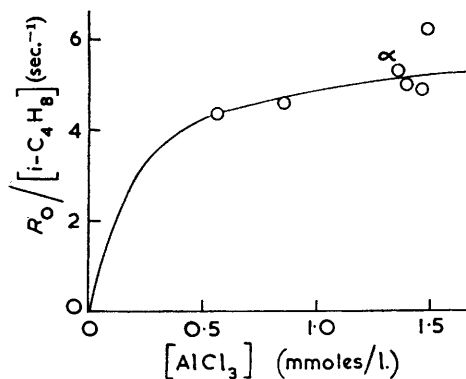


Fig. 2. The variation of $R_0/[\text{C}_4\text{H}_8]$ with aluminium trichloride concentration at -35°

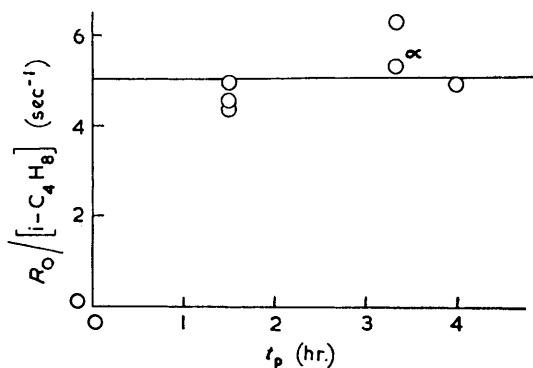


FIG. 3. The variation of $R_0/[\text{C}_4\text{H}_8]$ with pumping time at -35° .

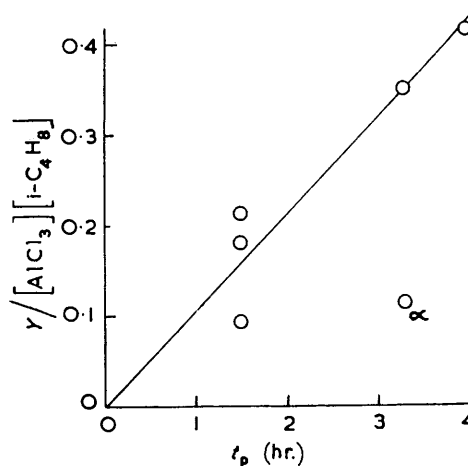


FIG. 4. The variation of the corrected yield with pumping time at -35° .

The yield of precipitable polymer, Y , is expressed as a percentage of the initial quantity of monomer.

necessarily meaningful. Nonetheless, it was found that the maximum reaction rate was proportional to the aluminium trichloride concentration over the range 0.7–2.2 mmoles/l., and independent of the pumping time (from 0.5 hr. without silane treatment of the apparatus, to 8 hr. with silane treatment).

As judged from the temperature rise, all these reactions went to completion, but the yield of high polymer that could be isolated ranged from 24 to 65%. The molecular weights ranged from 2000 to 3600.

Further proof that the reactions went to completion was obtained from experiments in which an additional phial of catalyst was broken; no further reaction took place. Also, on some occasions the temperature of the reaction mixture was lowered to about -30° (and in one experiment subsequently to -90°) after completion of the reaction, and further portions of monomer were then distilled into it. Each of these polymerised rapidly, and an almost quantitative yield of high polymer was obtained. In one such experiment, 8 ml. (88 mmoles) of isobutene was polymerised in 14 separate reactions in the same reaction mixture by 0.054 mmole of aluminium trichloride.

These experiments showed that the techniques which had enabled us to stop catalysis by titanium tetrachloride through intensive drying⁹ were inadequate to stop catalysis by aluminium trichloride. We therefore resorted to scavenging residual water by first breaking in the monomer solution a phial containing a solution of titanium tetrachloride in methylene dichloride. In each such experiment the extent of the ensuing reaction was negligibly small, showing the system to have been extremely dry; and each time the breaking of the aluminium trichloride phial caused rapid and complete polymerisation. In some of these experiments a quantity of triethylmethylammonium chloride approximately equivalent to the titanium tetrachloride was introduced (by breaking a phial) so as to remove this by complexing, before the aluminium trichloride phial was broken; this procedure did not prevent reaction.

In some other experiments the system was opened to the atmosphere during the reaction; this had no effect on the rate, whereas in reactions catalysed by titanium tetrachloride this would have effected a marked acceleration.

These experiments gave very strong indication that near 0° water is not required for the polymerisation of isobutene by aluminium trichloride in methylene dichloride.

Quantitative Experiments at -35° .—In these experiments a phial of aluminium trichloride was broken into the methylene dichloride, and approximately 15 min. was allowed for the catalyst to dissolve at about 0° . The temperature was then reduced to -35° and a phial containing a solution of isobutene in methylene dichloride was broken to start the reaction. Whilst this procedure removed the uncertainty concerning the effective catalyst concentration (except when this was relatively great; see below), it introduced the complication of an instantaneous, localised, high monomer concentration in the vicinity of the broken phial.

The results indicate that this effect was probably not serious. Fig. 1 shows that the initial rate, R_0 , is proportional to the isobutene concentration, and Fig. 2 that $R_0/[i-C_4H_8]$ is almost independent of the aluminium trichloride concentration over the range 0.6–1.5 mmoles/l.; an alternative interpretation is that $R_0/[i-C_4H_8] \propto [AlCl_3]^{0.2}$. Fig. 3 shows $R_0/[i-C_4H_8]$ to be independent of the pumping time, and thus of the water concentration. Figs. 1–4 include a point (α) representing an experiment in which a phial containing water was broken in the system after the aluminium trichloride had dissolved; it contained sufficient water to give a 0.48 mm-solution. Fig. 4 shows that a pumping time of 1 hr. leaves a water concentration in the system approximately equal to this. Fig. 4 also shows that the yield of polymer increases with the concentrations of monomer and catalyst, and with the pumping time. Since in these experiments, as in almost all others, the temperature record indicated that the reactions went to completion, it follows that, the greater the ratio $[H_2O]/[AlCl_3]$, the greater is the fraction of non-precipitable oligomers in the reaction product; in experiment α no precipitable polymer was obtained.

The formation of appreciable quantities of oligomers was first noted by Waterman, Over, and Tulleners,¹⁰ but was overlooked by later workers. It very largely deprives the molecular weight of the high polymers obtained simultaneously of any kinetic significance.

These experiments show that the reaction product of water and aluminium trichloride is a very effective chain breaker, and that the water concentration has no effect on the initial rate of polymerisation.

Quantitative Experiments at -60° .—These experiments were carried out by the same technique as those at -35° . In one set (the "wet" experiments) the pumping time was 0.5–1.5 hr., in the other ("dry") set the pumping time was 6–7 hr. (see Table).

Fig. 5 shows that the initial rate, R_0 , is independent of the monomer concentration, increases

⁹ (a) Longworth, Plesch, and Rutherford, *Proc. Chem. Soc.*, 1960, 68; *Doklady Akad. Nauk U.S.S.R.*, 1959, 127, 97. (b) Biddulph, Plesch, and Rutherford, *J.*, in the press.

¹⁰ Waterman, Over, and Tulleners, *Rec. trav. chim.*, 1934, 53, 699.

Experiments at -60° .

"Wet" experiments.

Expt.	25	22	10	16	9	11	24
$[i-C_4H_8]$ (mmoles/l.)	186	149	123	116	113	107	55.6
$[AlCl_3]$ (mmoles/l.)	1.83	5.12	1.07	2.86	1.15	1.17	0.60
t_p (hr.)	1.0	1.0	0.5	1.5	0.5	3.5	1.0
R_0 (mmole l. ⁻¹ sec. ⁻¹)	188	196	177	294	73.2	121	91.7
Y (%)	26	61	—	5.2	1.3	—	0.6
$10^{-3}M$	206	210	—	13.1	37.2	—	—

"Dry" experiments.

Expt.	26	27	30	21	17	15	19	23
$[i-C_4H_8]$ (mmoles/l.)	184	166	157	143	120	117	82.7	56.1
$[AlCl_3]$ (mmoles/l.)	1.91	0.48	13.29	7.50	1.00	3.01	1.19	0.53
t_p (hr.)	6.0	6.0	6.5	6.0	6.5	6.0	6.0	7.0
R_0 (mmole l. ⁻¹ sec. ⁻¹)	270	54	26	80	126	60	100	74
Y (%)	48	1.2	51	73	2.3	52	74	10.1
$10^{-3}M$	315.5	—	966	1,343	—	306	288	8.7

linearly with the concentration of aluminium trichloride to a maximum, and then falls, there being no significant difference between the "wet" and "dry" experiments, up to the maximum.

The reason for the maximum is not clear. It may be due to the solubility of aluminium trichloride in methylene dichloride at 0° being about 4 mm, so that at higher "nominal" concentrations some aluminium trichloride would remain undissolved. Thus, when the solution

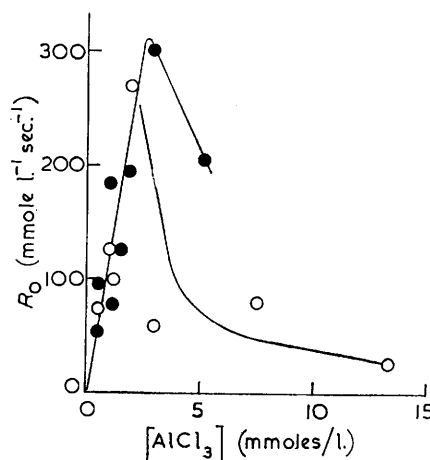


FIG. 5. The variation of R_0 with aluminium trichloride concentration at -60° .

$[C_4H_8]$ ranged from 55 to 186 mmoles/l. ○ "Dry" experiments; ● "wet" experiments.

was cooled to -60° excess aluminium trichloride could crystallise on the undissolved crystals, and the concentration of aluminium trichloride would be much lower than in the supersaturated solutions which may have been formed at lower nominal concentrations.

The information in Fig. 5 and the Table shows that up to the peak the ratio $R_0/[AlCl_3]$ is independent of monomer concentration. For the "wet" reactions the yield of polymer, Y , and the molecular weight, M , of those polymers, were significantly lower than for the "dry" reactions (see Table), thus confirming that water is, or produces, a chain-breaking agent, which was also shown by the experiments at -35° .

Experiments at -90° .—Two "wet" experiments (1.5 hr. pumping) at -94° gave virtually no polymer, whereas a "dry" experiment (8 hr. pumping), with $[C_4H_8] = 121$ and $[AlCl_3] = 2.2$ mmoles/l., gave a 100% yield of polymer of molecular weight 5×10^6 . These results are in concord with those obtained at the higher temperatures.

Temperature Dependence of Rate and Molecular Weight.—Since the kinetics of the reaction appear to change with temperature and we have but few results, it is not possible to calculate a meaningful activation energy of the rate. However, our results do show that at the same concentrations of monomer and catalyst, and with the same pumping time (water concentration), the rate of polymerisation decreases with fall in temperature. Our results also show that the

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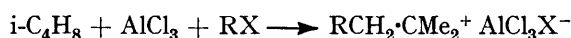
molecular weight increases as the temperature is reduced, but they are insufficient to provide a value of "activation energy of degree of polymerisation."

DISCUSSION

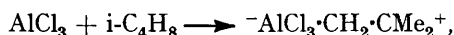
Our experiments show that water or its reaction product with aluminium trichloride is a very effective chain breaker. The large yields of high polymer obtained in the multiple monomer addition experiments can thus be explained on the basis that the residual water (or water-complex) is consumed during the polymerisation of the first portion of monomer, so that the polymerisation of the later additions probably took place in the absence of water. Similar highly efficient chain-breaking reactions due to water or to its reaction product with a metal halide have been recorded for many other systems.^{1,9b,11-14}

The results of the qualitative experiments indicate that water is not required for the polymerisation of isobutene by aluminium trichloride in methylene dichloride. Further evidence for this is afforded by the results of the quantitative experiments, in which it was observed that the water concentration had no marked effect on the rate of polymerisation. Three possible explanations can be offered for these findings:

- (1) Co-catalysis by an impurity, RX



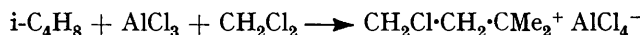
- (2) Direct initiation, either by the Hunter-Yohé mechanism¹⁵



or by a cation derived from self-ionisation of the catalyst¹⁶



- (3) Co-catalysis by the solvent



No conclusive proof against hypothesis (1) can be offered, but it seems unlikely to us because several batches of aluminium chloride phials were prepared and several batches of solvent were used, and there was no significant difference between results obtained with these. Moreover, if the reactions were due to co-catalysis by an impurity it must be one which is not a co-catalyst to titanium tetrachloride, and which is not consumed during the reaction. It can be shown that the reactions represented under (2) are both highly endothermic, even making a generous allowance for solvation energies, and this makes them rather unlikely.¹⁷ The third suggestion appears to us the most likely one, not only because analogous reactions are known,¹³ but because the energetics are favourable. The reaction need not be termolecular, since complexes of aluminium trichloride with both isobutene and methylene dichloride most probably exist under the relevant conditions, and the initiation would involve a bimolecular reaction of one, or both, of these.

Unfortunately, the mere presence of chlorine in the polyisobutenes would not prove

¹¹ Coombes and Eley, *J.*, **3700**, 1957.

¹² Overberger, Ehrig, and Marcus, *J. Amer. Chem. Soc.*, **1958**, **80**, 2456.

¹³ Colclough and Dainton, *Trans. Faraday Soc.*, **1958**, **54**, 886, 894.

¹⁴ Biddulph, Plesch, and Rutherford, International Symposium on Macromolecules, Wiesbaden, 1959, Paper III, A.10; Longworth and Plesch, *ibid.*, Paper III, A.11.

¹⁵ Hunter and Yohé, *J. Amer. Chem. Soc.*, **1933**, **55**, 1248.

¹⁶ Longworth and Plesch, *J.*, **1959**, 1887.

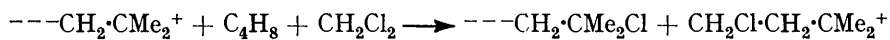
¹⁷ Plesch, in "Progress in High Polymers," Vol. 2, ed. Robb and Peaker, Heywood and Co. Ltd., London, in the press.

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solvent co-catalysis, because, by analogy with similar systems, a transfer reaction with solvent is highly probable:



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