31. *The Polymerisation of α-Methylstyrene catalysed by Stannic Chloride in Ethyl Chloride Solution.*

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An apparatus is described for the dilatometric measurement of the rate of polymerisation of α-methylstyrene by stannic chloride in carbon tetrachloride solution and for the quantitative separation of the dimer, trimer, tetramer, and pentamer from higher polymers produced. The infra-red absorption spectra and the chemical properties indicate that the polymers are saturated, and they are considered to possess a substituted phenylindane end group. Water is a co-catalyst, but the reaction rate is independent of the co-catalyst : catalyst concentration ratio when this quantity exceeds *ca.* 3. When D_2O is used as a co-catalyst the resultant polymer contains C–D linkages, and the initial reaction rate is lower than when H_2O is the co-catalyst; but the reaction then accelerates until it reaches the rate characteristic of the latter system. The rate of reaction is equal to $k_1[\text{SnCl}_4]^{3/2}[m_1]^y$, where y increases with m_1 from 1·2 towards 2, and $k_1 = k_1^{\circ} \exp(3{\cdot}5\ \text{kcal.}/\boldsymbol{R}T)$. The degree of polymerisation of the product is equal to $2 + k_2[m_1]$, where $k_2 = k_2^{\circ} \exp(4{\cdot}5\ \text{kcal.}/\boldsymbol{R}T)$. A reaction mechanism is proposed to account for these results, in which the initiation process is the abstraction of a proton by the monomer from the catalyst–co-catalyst complex. Growth of the polymer chain then follows by the usual carbonium-ion mechanism and the termination step is one of spontaneous proton release, which may be accompanied by cyclisation. It is concluded that $E_i = 1$ kcal., $E_t - E_p \doteqdot 4{\cdot}5$ kcal., and $A_p/A_t \doteqdot 1{\cdot}2 \times 10^{-3}$ l. mole^{-1}.

A STUDY of the polymerisation of α-methylstyrene induced by traces of Friedel–Crafts catalysts was undertaken for several reasons. First, the resonance stabilisation of the monomer due to conjugation of the aromatic nucleus with the ethylenic double bond, and the steric strain in the polymer due to αα′-disubstitution, are both factors which make for a low heat of polymerisation, and hence, if the entropy of this polymerisation has its normal value ($\Delta S^{\circ}_{\text{lsm}} \sim -30$ cal./deg. mole), the ceiling temperature (cf. Dainton and Ivin, *Trans. Faraday Soc.*, 1950, **46**, 331) should also be low. Some support for this view is provided by the fact that α-methylstyrene cannot be polymerised above ~80°. Accepting the above value of $\Delta S^{\circ}_{\text{lsm}}$, we deduce that, if $Tc_{\text{lsm}} \sim 350°$ K, then $\Delta H_{\text{lsm}} < 10$ kcal. Jessup and Roberts (cited by Roberts, *J. Res. Nat. Bur. Stand.*, 1949, **44**, 221) have recently measured the heat of conversion of liquid monomer into various polymers of low molecular weight and has obtained values of 10 kcal. for an average degree of polymerisation of 7·6. α-Methylstyrene therefore seemed to be a suitable monomer for investigating propagation–depropagation equilibria in cationic polymerisation. Secondly, the results of the earlier workers indicated that low-molecular-weight products are formed at room temperature, and this condition is favourable to the application of infra-red spectroscopic methods for the detection of end-groups. Thirdly, according to Pepper's work (*Trans. Faraday Soc.*, 1949, **45**, 425), the reaction is sensitive to changes of dielectric constant of the medium and insensitive to moisture, and the molecular weight of the polymer can be determined by addition of bromine to the double bond at the end of each polymer chain. The results of our preliminary experiments were so different from those of previous workers that the original objects of the investigation were modified so as to become merely the exploration of the kinetics of the polymerisation in ethyl chloride solution of α-methylstyrene catalysed by stannic chloride, care being taken to handle all chemicals *in vacuo* with carefully controlled quantities of added water, to measure initial reaction rates dilatometrically, and to investigate both the molecular weight and the structure of the polymers formed.

EXPERIMENTAL

(a) *Materials.*—α-Methylstyrene, given by the Distillers Company Ltd., was stored over nitrogen. Before use it was degassed and distilled twice *in vacuo*, only the middle third fraction being kept each time. Ethyl chloride, supplied by B.D.H. Ltd., was dried [$\text{Mg(ClO}_4)_2$], outgassed by pumping and freezing, and distilled from the perchlorate at the temperature of solid carbon dioxide to a storage trap surrounded by liquid air. Only the first two-thirds of the distillate was retained. Stannic chloride was outgassed and distilled *in vacuo*, only the third quarter of the distillate being returned.

All chemicals were handled *in vacuo* throughout.

(b) *Dilatometers.*—These consisted of bulbs made from 8-mm. Pyrex tubing joined to precision capillary tubing of uniform cross-sectional area = 0·776 mm.². Within each dilatometer bulb was a magnetic stirrer made of iron wire sealed in glass tubing, which could be alternately raised and lowered by a solenoidal magnet fitting concentrically over the dilatometer bulb. Because of the closeness of fit of the stirrer to the dilatometer bulb wall, the dilatometer was slightly warmer than the thermostat. This heating effect was constant throughout any one run and could be evaluated by observing the meniscus rise associated with the stirring. In no case was the effective temperature of the dilatometer more than 0·1° above that of the thermostat.

(c) *Procedure.*—In order to fill the dilatometer and bring the monomer and catalyst together at exactly the right temperature, the following procedure was adopted : (i) The monomer was distilled into a graduated tube, and from there a known volume was distilled into the bottom of the dilatometer ; once in the dilatometer, the α-methylstyrene was frozen and kept at liquid-air temperature until the start of the run. (ii) If water was to be added, this was distilled into the dilatometer next (see stannic chloride, below). (iii) The amount of ethyl chloride required to fill the dilatometer to a suitable level at the temperature of the experiment was then added : this was measured as vapour in a calibrated volume at known temperature and pressure. For dry runs or runs containing known quantities of added water, a sample of the ethyl chloride from the storage trap was condensed and evaporated several times from magnesium perchlorate at −78°. (iv) The stannic chloride catalyst was distilled into the dilatometer on top of the frozen ethyl chloride. The stannic chloride and the added water were measured by their respective pressures in a known volume. A glass Bourdon gauge was used as manometer. For experiments at very low catalyst concentrations (less than 4×10^{-1}M) the catalyst was premixed with ethyl chloride vapour in the ratio of 1 : 5 before measurement. (v) Whilst the monomer was kept frozen at the bottom of the dilatometer, the catalyst was mixed with approximately half the solvent by melting the ethyl chloride in the top part of the dilatometer. In this way it was possible to prevent the catalyst from concentrating in the capillary when the dilatometer was immersed into the thermostat.

The dilatometer was sealed *in vacuo* and kept in liquid air until required.

At the start of a run the dilatometer was completely immersed in a thermostat. No reaction could take place while temperature equilibrium was being reached since a thick layer of solvent separated the monomer from the catalyst. The initial reading of the miniscus was then taken, and the reaction started by setting the magnetic stirrer in motion. There was a slight volume change when the components were mixed which caused an error in the initial reading so obtained. In view of this, and in order to hasten the attainment of thermal equilibrium, the stirrer was started before thermal equilibrium was reached. This also reduced the possibility of any adventitious mixing of the monomer and catalyst. This method being used, the initial reading could be obtained with the aid of a slight extrapolation.

(d) *Polymer.*—In the majority of runs the reaction was carried to completion. The pure polymer from a given run was obtained by cutting off the top of the dilatometer, inverting it, and gently warming the dilatometer bulb. The boiling of the ethyl chloride then forced the contents of the dilatometer into a receiver. The solvent was removed from the polymer by evaporation at room temperature, followed by pumping to remove the final traces.

The polymers of low molecular weight were quantitatively separated as follows : About 0·3 g. of polymer was placed at the closed end of a horizontal Pyrex tube about 150 cm. long, made from 14-mm. bore tubing and containing constrictions every 3—4 cm. in order to prevent liquid flow along its length. This tube was then connected to the high-vacuum system in a horizontal position by means of a standard taper joint and evacuated. Around the glass tube was placed a heavy-walled copper tube, which was heated electrically to approximately 160° at the end containing the polymer and water-cooled at the opposite end. After several hours distinct bands of dimer, trimer, and tetramer were obtained along the length of the glass tube. The fractions were estimated by cutting the glass tube and weighing the sections. There were no signs of depolymerisation of the polymer when heated under these conditions.

(e) *Initial Rate of Shrinkage.*—For most of the experimental results the difference (x) between the dilatometric reading at any instant and the reading when the reaction had proceeded to completion decreased exponentially with time (t) according to the relation $x = x_0 e^{-kt}$, where x_0 is the total movement of the meniscus during the reaction. The dilatometric readings over the first 2 minutes, during which thermal equilibrium was disturbed by the stirring and then re-established, were sometimes in error, and in these cases the initial shrinkage rate was taken to be kx_0, since both k and x_0 could be accurately determined, from the dilatometer reading taken before stirring was begun and those taken subsequently.

(f) *Initial Rate of Reaction.*—If the polymer being formed throughout a given reaction has a constant density (due to constant composition or other cause) the shrinkage factor, defined as the concentration of monomer polymerised per unit length of meniscus movement, is equal to $[m_1]_0/x_0$, where $[m_1]_0$ is the initial value of the monomer concentration. It was not expected that this condition would be satisfied, since the di-, tri-, tetra-, and penta-mers differ considerably in density and are formed at different rates which vary as the reaction proceeds. However, estimates of the initial shrinkage factor based on comparison of the extent of meniscus fall for low known percentage conversions differed only slightly from $[m_1]_0/x_0$, *e.g.*, by 2%. Since errors of this magnitude are within the experimental error, it was considered reasonable to take $[m_1]_0/x_0$ as representing the true shrinkage factor.

(g) *Molecular Weights.*—The number-average molecular weights were determined cryoscopically in benzene or by calculation from the weight percentages of the various polymers when these components had been separated by the method described in section (d). The two methods gave comparable results. In some cases it was possible to analyse the polymer formed at several stages during a run and hence to extrapolate backwards to obtain an approximate value of the average molecular weight of the polymer forming at the start of the reaction.

(h) *Infra-red Spectra.*—Measurements were made with a Perkin–Elmer single-beam instrument by Dr. N. Sheppard, using methods appropriate to polymers of low molecular weight which are either liquid at room temperature or melt just above room temperature.

Results.—(a) *Properties of the polymers.* In general the properties of the various isolated polymers were as described by Staudinger and Breusch (*Ber.*, 1929, **62**, 442) except that the values of the refractive indices obtained by us were all about 0·002 unit higher than theirs. The dimer was a white crystalline solid, m. p. 52·0°, the melt of which supercooled to a much less dense liquid of n_D^{20} 1·5652 which was extremely reluctant to crystallise without seeding. The trimer was a clear amorphous solid, n_D^{20} 1·5875, which formed a viscous liquid at 25°. All the higher polymers were amorphous solids at room temperature.

The cryoscopically determined molecular weights of the various isolated polymers were exact multiples of the molecular weight of the monomer and therefore could not have contained adsorbed catalyst or chemically combined fragments of catalyst. No signs of unsaturation were detected in the polymer. Thus it did not enter into addition reactions, and the infra-red absorption spectrum showed no absorption in the regions characteristic of olefinic double bonds. The polymer was quite stable in the presence of the catalyst, neither undergoing further polymerisation, nor, if heated, depolymerising. This stability was not due to inactivation of the catalyst, which displayed its normal power of polymerising added monomer. Quite apart from the theoretical significance of these results (see p. 159), the saturated character of the polymer indicates that bromination is likely to be a highly unsuitable method for determining polymer molecular weights. Pepper, who used somewhat similar experimental conditions, obtained very erratic results by the bromination method, and we therefore think that his

TABLE 1. *Effect of water on rate of polymerisation of α-methylstyrene at 55°.*

(α-Methylstyrene, 0·56M; $SnCl_4$, 8·1 × 10^{-4}M; shrinkage factor, 0·0910.)

	Methods of drying: *		H_2O added,	Initial rate, 10^{-3} mole		Methods of drying: *		H_2O added,	Initial rate, 10^{-3} mole
Expt.	EtCl	Monomer	10^{-4} mole l.$^{-1}$	l.$^{-1}$ min.$^{-1}$	Expt.	EtCl	Monomer	10^{-4} mole l.$^{-1}$	l.$^{-1}$ min.$^{-1}$
32	A	—	—	7·50	49	C	—	—	2·50
33	A	—	—	7·68	47	C	—	4·1	11·3
36	A	—	16·0	7·68	44	C	—	8·1	9·2
37	A; also B	S	—	3·42	45	C	—	8·1	9·0
41	C	S	—	2·84	52	C	—	16·0	11·5
42	C	—	—	3·58	43	C	—	24·5	7·30
46	C	—	—	4·60	51	C	—	39·7	7·45
48	C	—	—	2·00	53	C	—	78·5	8·40

* (A) Distilled from solid CO_2 to liquid air. (B) Condensed and evaporated from P_2O_5 several times. (C) As for Expt. 37 except that $Mg(ClO_4)_2$ was used instead of P_2O_5. (S) Silica gel.

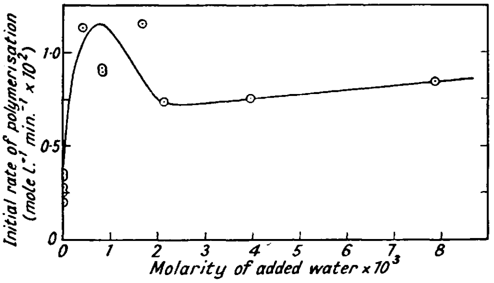
conclusions, based on this method, as to the dependence of the molecular weight of the polymer on the dielectric constant should be accepted with reserve.

(b) *Effect of water on the rate of polymerisation.* A series of experiments was carried out at 55° to determine the effect of added water on the rate of polymerisation. The experimental results are given in Table 1 and shown graphically in Fig. 1. Although the exact concentration of water in Expts. 32, 33, and 36 is not known, it seems reasonable to assume that it exceeded 5×10^{-3}M in view of the relatively ineffective method of drying the ethyl chloride.

The results show that water is probably a co-catalyst, and that as the drying is intensified the results become less reproducible. The latter feature is, no doubt, due to traces of remaining water, and it appears possible that no reaction would occur at all in a completely anhydrous system, as in the case of *iso*butene (Evans and Meadows, *Trans. Faraday Soc.*, 1950, **46**, 327). When the ratio of added water to catalyst concentration is greater than about 3 : 1 the initial rate of polymerisation becomes independent of the amount of water present.

(c) *Effect of added deuterium oxide.* Further information concerning the mechanism of the co-catalytic action of water was obtained from experiments in which D_2O was used in place of H_2O. The infra-red absorption spectra of the pure trimers obtained in the presence of the two waters were compared. The two types of spectra were identical except for an absorption band at 2180 cm.$^{-1}$ in the case of polymers formed in the presence of the D_2O. Since this is the frequency associated with the carbon–deuterium bond, it is assumed that some of the deuterium from the D_2O was incorporated into the polymer. This indicates that the initiating stage of the polymerisation is the donation of a proton (or deuteron) to the double bond of the monomer (cf. Dainton and Sutherland, *J. Polymer Sci.*, 1949, **4**, 37).

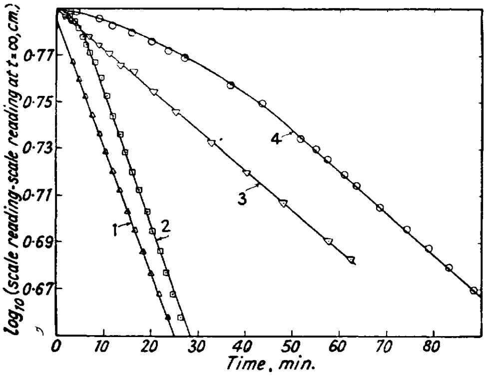
FIG. 1. *The effect of added water on the rate.*



$[m_1]_0 = 0{\cdot}56$M, $[SnCl_4]_0 = 0{\cdot}81 \times 10^{-3}$M, $T = 55°$ c.

Note that three other experiments, corresponding to an estimated water content greater than 5×10^{-3}M but which was not known with precision, gave rates of 0·752, 0·768, and $0{\cdot}768 \times 10^{-2}$ mole l.$^{-1}$.

FIG. 2. *The effect of added deuterium oxide on the rate.*



$[m_1]_0 = 0{\cdot}56$M, $T = 55°$c.

Curve 1 : $[SnCl_4]_0 = 0{\cdot}81 \times 10^{-3}$M; $[H_2O]_0 = 1{\cdot}9 \times 10^{-3}$M.
,, 2 : $[SnCl_4]_0 = 0{\cdot}81 \times 10^{-3}$M; $[D_2O]_0 = 3{\cdot}95 \times 10^{-3}$M.
,, 3 : $[SnCl_4]_0 = 0{\cdot}40 \times 10^{-3}$M; $[H_2O]_0 = 3{\cdot}90 \times 10^{-3}$M.
,, 4 : $[SnCl_4]_0 = 0{\cdot}40 \times 10^{-3}$M; $[D_2O]_0 = 3{\cdot}95 \times 10^{-3}$M.

The use of D_2O in place of H_2O as a co-catalyst modified the shrinkage rate in the first stages of the reaction, as illustrated by some typical curves in Fig. 2. The initial shrinkage rate is evidently less when D_2O is used than when H_2O is used, but the reaction accelerates and ultimately attains the rate characteristic of H_2O as a co-catalyst. It was at first considered possible that the cause of the acceleration was the destruction of some retarder in the D_2O. This explanation was rendered less likely by the fact that a fresh sample of 99·75% D_2O, which had previously been unopened and came from a different source, produced the same effect. It is hoped to study this phenomenon in greater detail later. For the present we tentatively regard it as a genuine isotopic effect, since, if it is true that the $SnCl_4$–D_2O complex initiates the polymerisation more slowly than the $SnCl_4$–H_2O complex, the acceleration can be accounted for. Any reaction mechanism which satisfies the minimum requirements of proton initiation and catalyst regeneration leads to the conclusion that the D_2O must be converted into H_2O, and therefore that the reaction with D_2O as co-catalyst must continue to accelerate until all the D_2O has been so converted whereupon the rate characteristic of H_2O as co-catalyst will be reached but not exceeded. A corollary to this conclusion is that the number of molecules of polymer formed by the time the rate characteristic of H_2O as co-catalyst has been reached must exceed the number of D_2O molecules which was originally present in the catalyst–co-catalyst complex. This was always true. For example, in the experiment corresponding to curve 4 of Fig. 2, $3{\cdot}95 \times 10^{-5}$ mole of D_2O was originally present, and by the time the normal rate had been reached $\sim 7 \times 10^{-5}$ mole of polymer had been formed.

There is a little evidence that this effect of D_2O in reducing the rate in the early stages of the reaction reaches a maximum as more D_2O is added. Such a result would not be inconsistent with the saturation effect (Fig. 1) of H_2O on the rate. Both these phenomena can be accounted for if it is assumed that only a certain ratio of co-catalyst to catalyst is necessary for the reaction to attain its maximum rate, and that any additional water in excess of this ratio is not only redundant but for some unknown reason, which might be physical inhomogeneity, is unable to exchange protons with the water chemically bound to the catalyst.

(d) *Effect of catalyst–co-catalyst concentration.* It was soon evident that an increase of catalyst concentration caused a more than proportionate increase in the reaction rate, and experiments were therefore designed to determine the order with respect to catalyst concentration at several temperatures and as far as possible with sufficient co-catalyst present to ensure that slight variations of catalyst–co-catalyst ratio did not affect the rate, *i.e.*, in the level portion of Fig. 1. The results are summarised in Fig. 3, from which it is seen that at 0° the order is 1·54, at 25° it is 1·42, and at 55° 1·60. Whereas some of the points on curves 2 and 3 of Fig. 3 correspond to unknown water concentrations, the water content for all the experiments corresponding to points on Curve 1 was precisely known. We therefore conclude that at 0° and 0·56M-monomer, the order is 1·5 with respect to catalyst, and that this order probably prevails at other temperatures and monomer concentrations.

The effect of catalyst and co-catalyst concentration on the molecular weight of the polymer produced was investigated at 55°, a concentration of monomer of 0·56M being used. The results are given in Table 2, from which it may be seen that, although the initial rate varied by a factor of 7, the molecular weight was constant, corresponding to a degree of polymerisation of 2·5. This series of experiments, together with the molecular-weight data of other experiments not specifically designed to test this point, establish that for a given monomer concentration and temperature the degree of polymerisation is independent of the catalyst–co-catalyst concentration.

TABLE 2. *The effect of catalyst and co-catalyst concentration on the degree of polymerisation.* (*Monomer concentration* = 0·56M; *temp.* 55°.)

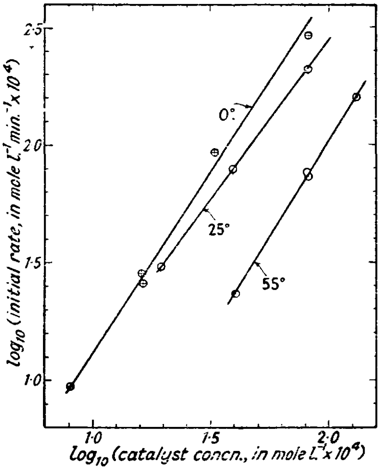
Catalyst concn., 10^{-4} mole $l.^{-1}$	Added H_2O, mole $l.^{-1}$	Initial rate, 10^{-3} mole $l.^{-1}$ $min.^{-1}$	Mol. wt. of polymer	Catalyst concn., 10^{-4} mole $l.^{-1}$	Added H_2O, mole $l.^{-1}$	Initial rate, 10^{-3} mole $l.^{-1}$ $min.^{-1}$	Mol. wt. of polymer
4·05	$3{\cdot}9 \times 10^{-3}$	2·36	298	8·10	$8{\cdot}1 \times 10^{-4}$	9·0	289 *
8·10	Normal drying	7·68	293	8·10	$4{\cdot}0 \times 10^{-4}$	11·3	298 *
8·10	Rigorous ,,	3·42	295	13·10	Normal drying	16·1	292
8·10	,, ,,	2·84	293				

* Determined cryoscopically, the remainder by polymer analysis (see p. 152).

In all those experiments for which the number-average molecular weight of the polymer was measured, the ratio of the number of polymer molecules formed to the number of catalyst or co-catalyst molecules originally present greatly exceeded unity and in some cases was greater than 10^3.

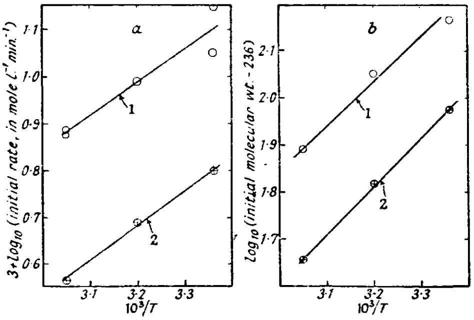
(e) *Effect of monomer concentration.* A change of the monomer concentration affects both the molecular weight of the polymer and the rate of reaction. Since the degree of polymerisation is low and the relative shrinkage factors corresponding to formation of dimer, trimer, tetramer, and pentamer calculated from Staudinger's density data are in the ratio 1·00 : 1·35 : 1·44 : 1·45, the analysis of shrinkage–time curves at different monomer concentrations required a knowledge of the polymer composition–time curves. It was for this purpose that the polymer analysis procedure described in section (g) (p. 153) was devised. Although this procedure was accurate, it was too time-consuming to allow of obtaining a molecular weight distribution curve for successive stages of reaction for a series of experiments covering the whole range of conditions. Two expedients were therefore decided upon : (*a*) to analyse the polymer formed at low and at complete conversion in order to discover to what extent the number-average molecular weight changed throughout reaction, and (*b*) to investigate the reaction at lower temperatures under conditions where the higher molecular weights of the polymers formed would ensure a constant shrinkage factor during reaction. Experiments of the latter type will be reported in a later publication. Table 3 illustrates the type of result obtained by experiments of the first type, and it will be seen that the molecular weight increases with monomer concentration. A feature of the graphs of initial molecular weight against monomer concentration is that if straight lines are drawn through the points the molecular weight at zero monomer concentration is always that of the dimer, irrespective of the temperature.

FIG. 3. *The effect of catalyst concentration on the rate at different temperatures.*



$[m_1]_0 = 0{\cdot}56$M ; $[H_2O]_0/[SnCl_4]_0 \geqslant 3$.

FIG. 4. *The effect of temperature on* (a) *initial rate and* (b) *the molecular weight of the polymer formed in the initial stages of reaction.*



Curves 1, $[m_1]_0 = 0{\cdot}56$M.
Curves 2, $[m_1]_0 = 0{\cdot}32$M.

TABLE 3. *Effect of monomer concentration and temperature on the composition and molecular weight of polymer.*

Catalyst concn., $8{\cdot}1 \times 10^{-4}$M.

Temp.	Monomer concn., mole $l.^{-1}$	Polymer analysis, mol. % of : * (2)	(3)	(4)	(5)	(x)	M at 100% reaction	Approx. initial M
0°	0·56	—	—	—	—	—	415 †	—
25	0·32	29·0	62·0	9·0	—	—	330	330
25	0·56	18·0	71·0	10·0	1·0	—	347	384
25	0·56	15·0	72·0	12·0	1·0	—	356 ‡	—
25	0·80	15·0	65·0	9·0	9·0	2·0	374	453
40	0·32	46·0	51·0	3·0	—	—	303	303
40	0·56	30·5	68·5	1·0	—	—	323	350
55	0·32	62·5	37·5	—	—	—	281	281
55	0·56	51·5	48·5	—	—	—	293	313
55	0·56	50·5	49·5	—	—	—	295	315
55	0·56	—	—	—	—	—	289 †	—
55	0·56	—	—	—	—	—	298 †	—
100	0·56	88·0	12·0	—	—	—	251	—

* (2) = Dimer, (3) = trimer, (4) = tetramer, (5) = pentamer, (x) = high polymer.
† Determined cryoscopically. ‡ Analysis for 75% reaction.

The effect of monomer concentration on the initial rate, expressed as moles of monomer consumed per l. per min., is given in Table 4, due allowance having been made for the different shrinkage factors appropriate to the initial phases of each reaction. The values at 0° indicate an order with respect to monomer of unity at low concentrations which increases at higher concentrations and finally above 0·8M-concentration decreases again. This variation is outside the limits of experimental error. Although the same concentration range has not been covered, the data at other temperatures are more consistent with an order of unity at low concentrations, rising above this value as the monomer concentration is increased, the average value of the order over the range studied being 1·4.

(f) *Effect of temperature.* From data already presented it can be seen that both the rate of reaction and the molecular weight of the polymer decrease with increasing temperature. In Fig. 4 log (initial rate) and log (amount by which molecular weight of the polymer formed initially exceeds that of the dimer) for two different concentrations of monomer (0·32 and 0·56M) have been plotted against the reciprocal of the absolute temperature. The straight lines correspond to apparent Arrhenius energies of $E \sim -3{\cdot}5$ kcal. for the rates and $E_M \sim -4{\cdot}5$ kcal. for the molecular weights. The vertical displacements of the lines correspond to an order with respect to monomer of 4/3 and a direct proportionality between molecular weight and monomer concentration at any given temperature.

TABLE 4. *Effect of monomer concentration on initial rate of reaction at various temperatures.*

Temp.	Monomer concn., mole $l.^{-1}$	Catalyst concn., 10^{-4} mole $l.^{-1}$	Initial rate, 10^{-3} mole $l.^{-1}$ $min.^{-1}$
0°	0·32	1·62 *	1·73
0	0·40	1·62 *	2·20
0	0·56	1·62 *	2·84
0	0·56	1·62 *	2·56
0	0·68	1·62 *	6·71
0	0·80	1·62 *	10·6
0	1·20	1·62 *	18·3
0	1·92	1·62 *	19·4
25	0·32	8·1	6·25
25	0·40	8·1	7·03
25°	0·56	8·1	11·2
25	0·56	8·1	14·1
25	0·80	8·1	21·2
40	0·32	8·1	4·9
40	0·56	8·1	9·69
55	0·32	8·1	3·67
55	0·56	8·1	7·50
55	0·56	8·1	7·68
55	0·56	8·1 †	7·30

* Added water, 1·62 × 10^{-3}M.

† Added water, 2·1 × 10^{-3}M.

Other interesting features of the effect of temperature, clearly seen in Table 3, are that: (i) high polymers (*i.e.*, larger than the pentamer) are not formed at all at initial monomer concentrations below about 0·7M and temperatures greater than 25°, (ii) pentamers are not formed at 40° and higher temperatures for $[m_1]_0 < 0{\cdot}56$M; (iii) at 55° tetramers cease to be formed, whereas (iv) trimers and dimers are formed up to at least 100°.

DISCUSSION

The kinetics of this reaction may be summarised by the equations:

$$-d[m_1]/dt = k_1[\mathrm{SnCl_4}]^{3/2}[m_1]^y \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and

$$\overline{\mathrm{DP}}_0 = 2 + k_2[m_1]_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where $[m_1]$ denotes monomer concentration; y increases from unity at low concentrations to higher values at higher concentrations; $k_1 = k_1{}^{\circ} \exp(3{\cdot}5 \text{ kcal.}/\boldsymbol{R}T)$; $k_2 = k_2{}^{\circ} \exp(4{\cdot}5 \text{ kcal.}/\boldsymbol{R}T)$ and is independent of $[\mathrm{SnCl_4}]$ under the conditions used, and $\overline{\mathrm{DP}}_0$ is the number-average degree of polymerisation corresponding to $[m_1]_0$. Water is an essential co-catalyst, and k_1 is therefore a function of $[\mathrm{H_2O}]$. However, provided the concentration of water is greater than roughly 3 times the catalyst concentration, which is the state of affairs when the usual methods of drying are employed, k_1 and the reaction rate are independent of $[\mathrm{H_2O}]$. The role of the co-catalyst is revealed by using D_2O as the catalyst, when C–D bonds are detected in the resultant polymer. It is concluded that the co-catalyst combines with the $SnCl_4$ to form a compound of unspecified formula which initiates polymerisation by donating a proton to a monomer molecule, thereby converting the latter into a carbonium ion of probable formula $(CH_3)_2\overset{+}{C}{\cdot}C_6H_5$. The fact that the number of polymer molecules formed in a reaction greatly exceeds the number of co-catalyst molecules initially present implies that the latter are regenerated, and that the termination reaction is one of proton expulsion, the proton being ultimately returned to an anionic fragment of the catalyst–co-catalyst compound. The lag phase observed when D_2O is used as a co-catalyst is in harmony with this mechanism. Two conclusions may be drawn from the results expressed in equation (2) : (*a*) that chain transfer to monomer does not occur, and (*b*) that the rate of the proton-repulsion process involved in chain termination is independent of both the catalyst and monomer concentrations. We may therefore write the reaction mechanism in the form

$$\text{Initiation}: \ \mathrm{A} + m_1 \longrightarrow \mathrm{A}^- + m_1^+ \ (k_i) \quad . \ . \ . \ . \ . \quad (3)$$

$$\text{Propagation}: \ m_1^+ m_j^+ \longrightarrow m^+{}_{j+1} \ (k_{p,j}) \quad . \ . \ . \ . \ . \quad (4)$$

$$\text{Termination}: \ m_j^+ \longrightarrow \mathrm{H}^+ + \mathrm{P}_j \ (k_{t,j}) \quad . \ . \ . \ . \ . \quad (5)$$

where m_1 denotes monomer, A the catalyst–co-catalyst complex providing the protons, m_j^+ the growing polymer carbonium ion containing j monomeric segments, and P_j the dead polymer containing j monomeric units. The most obvious objection to this simple scheme is that it predicts that the reaction rate will be proportional to [A], and it is natural to assume that [A] is in turn proportional to an integral power of the catalyst concentration. However, the observed exponent of the catalyst concentration in the expression for the rate is 1·5. This exponent is the most unusual feature of the reaction, since in most ionic polymerisations the exponent is unity. In one case where it exceeds unity, namely, the iodine-catalysed polymerisation of octyl vinyl ether (Eley and Richards, *Trans. Faraday Soc.*, 1949, **45**, 425), the observed exponent of 2 was readily accounted for by assuming the chain initiator to be the I^+ ion in equilibrium with iodine molecules according to $2\mathrm{I}_2 \rightleftharpoons \mathrm{I}^+ + \mathrm{I}_3^-$. In the present case the corresponding equilibrium might be

$$3\mathrm{SnCl}_4 + 2\mathrm{H}_2\mathrm{O} \rightleftharpoons 2\mathrm{H}^+ + \mathrm{Sn}_3\mathrm{Cl}_{12}(\mathrm{OH})_2 \quad . \ . \ . \ . \ . \ . \quad (6)$$

and a plausible structure for the anion is readily formulated. However, no special significance can be attached to equation (6), and for the present we merely write $[\mathrm{A}] = K[\mathrm{SnCl}_4]^{2/3}$, in order to satisfy equation (1). The expression for the reaction rate deduced from the mechanism is

$$-\frac{\mathrm{d}[m_1]}{\mathrm{d}t} = k_i[m_1][\mathrm{A}]\,\frac{k_{p_1}[m_1]}{k_{p_1}[m_1] + k_{t_1}}\left\{2 + \sum_{j=1}^{j=\infty} \pi\left(\frac{k_{p,j}[m_1]}{k_{p,j+1}[m_1] + k_{t,j+1}}\right)\right\} \quad . \quad (7)$$

and if we assume that the velocity constants k_p and k_t are independent of j, this becomes by summation of the convergent series

$$-\frac{\mathrm{d}[m_1]}{\mathrm{d}t} = k_i[m_1][\mathrm{A}]\,\frac{k_p[m_1]}{k_p[m_1] + k_t}\left\{1 + \frac{1}{1 - \dfrac{k_p[m_1]}{k_p[m_1] + k_t}}\right\}$$

$$= k_i[m_1][\mathrm{A}]\,\frac{k_p[m_1]}{k_p[m_1] + k_t}\left\{2 + \frac{k_p[m_1]}{k_t}\right\} \quad . \quad (8)$$

When high polymers are formed $k_p[m_1] \gg k_t$, and equation (8) reduces to the familiar form

$$-\mathrm{d}[m_1]/\mathrm{d}t = (k_i k_p/k_t)[\mathrm{A}][m_1]^2$$

However, the reaction is of less than second order with respect to monomer, and this is due to the fact that only polymers of low molecular weight are formed so that $k_p[m_1]$ is of the same order of magnitude as k_t. On closer examination equation (8) is seen not to express the observed variation of the rate with change of monomer concentration. Much closer accord with experiment may be achieved by omitting k_t from the term outside the bracket. It will be recalled that this k_t is really k_{t_1} [of equation (7)], and putting it equal to zero is equivalent to stating that the monomeric ion m_1^+ does not spontaneously expel a proton and that either (*a*) all monomeric ions formed in the initiation reaction react to form a dimer, or (*b*) a large proportion revert to $\mathrm{A} + m_1$. The two cases (*a*) and (*b*) correspond to values of $[m_1^+]$ of $k_i[\mathrm{A}]/k_{p_1}$ and $(K[\mathrm{A}][m_1])^{\frac{1}{2}}$, respectively, where K is the equilibrium constant of the ionisation reaction (3). The present data do not permit a decision between these two possibilities, although the data at 0° suggest that the order with respect to monomer may exceed 1·5. Writing $V_{\text{init.}}$ for reaction (3), thereby deliberately leaving open the question of the initiation mechanism, we find for the rate equation

$$-\mathrm{d}(m_1)/\mathrm{d}t = V_{\text{init.}}\{2 + k_p(m_1)/k_t\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

from which we deduce

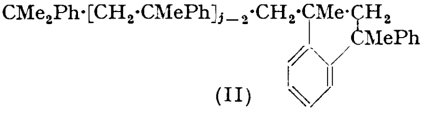
$$\overline{\mathrm{DP}}_0 = [2 + k_p(m_1)]/k_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The rather meagre data available are in accord with equation (11) and may be used to show that $E_t - E_p = 4{\cdot}5$ kcal. and $k_p/k_t = 1{\cdot}2 \times 10^{-3} \,.\, \exp(4{\cdot}5/\boldsymbol{R}T)$ l. mole^{-1}. The apparent overall activation energy E_R should, according to equation (10), decrease from a value $= E_i + \frac{1}{2}\Delta H_6$ at low monomer concentrations to a limiting value of $E_i + \frac{1}{2}\Delta H_6 + (E_p - E_t)$ at higher monomer concentrations. The observed value of E_R is $-3{\cdot}5$ kcal., and therefore the maximum value of $E_i + \frac{1}{2}\Delta H_6$ is 1 kcal., which, although small, is not inconsistent with the findings in other ionic polymerisations; *e.g.*, Plesch (*Sci. Proc. Roy. Dublin Soc.*, 1950, **25**, 154) has found that the highest possible value of E_i in the $TiCl_4$–H_2O-catalysed polymerisation of *iso*butene is 4 kcal., and the probable value is much smaller.

In the foregoing paragraphs no reference has been made to the saturated structure of the polymer formed. When Tiffeneau (*Ann. Chim. Phys.*, 1907, **10**, 158) first prepared the saturated dimer of α-methylstyrene, he concluded that it was 1 : 3-dimethyl-1 : 3-diphenyl*cyclo*butane. Staudinger and Breusch concurred in this view and also concluded that the higher polymers which they isolated were large alicyclic compounds. More recently, Bergmann, Taubadel, and Weiss (*Ber.*, 1931, **64**, 1493) re-examined the saturated dimer and concluded that it is in fact 1 : 1 : 3-trimethyl-3-phenylindane, suggesting that formation of the saturated dimer proceeded *via* the unsaturated dimer, 1 : 3 : 3-trimethyl-1 : 3-diphenylpropene [4-methyl-2 : 4-diphenylpent-2-ene].

There is also little doubt that under suitable conditions unsaturated polymers of α-methylstyrene can be prepared by using, *e.g.*, phosphoric acid, floridin (Klages, *Ber.*, 1902, **35**, 2639; Lebedev and Filonenko, *Ber.*, 1925, **58**, *B*, 163), or even stannic chloride as catalyst. These facts can be reconciled by regarding the normal fast termination reaction as proton expulsion from the β-carbon atom to form the unsaturated polymer (I) which is capable of rearrangement to form a saturated polymer (II) containing a 1 : 3-dimethyl-3-phenylindanyl end group :

$$\begin{array}{c} \mathrm{CMe_2Ph{\cdot}[CH_2{\cdot}CMePh]_{\mathit{j}-1}{\cdot}CH{:}CMePh + H^+} \quad \text{(I)} \\ \downarrow \\ \mathrm{CMe_2Ph{\cdot}[CH_2{\cdot}CMePh]_{\mathit{j}}^{+}} \quad \text{(III)} \end{array}$$



(II)

It would be expected that this rearrangement would be catalysed by the catalyst–co-catalyst complex [possibly proceeding *via* the carbonium ion (III)], and if the energy of activation is appreciable the proportion of unsaturated polymer formed would be larger the lower the temperature. Although no quantitative data exist for adequate testing of this prediction, it is in harmony with the qualitative data available.

The possibility that D_2O is a less effective co-catalyst than H_2O has been mentioned and, in view of the reaction mechanism proposed, the difference is probably due to the different rates of abstraction by the monomer of H^+ and D^+ from the catalyst–co-catalyst complex. Although isotopic influences of this kind have not hitherto been observed in ionic polymerisations, they have been recognised in acid–base catalysis (Bell, " Acid Base Catalysis," Oxford, 1949, pp. 143—152). It is hoped to investigate this aspect of the reaction in detail later.

The very steep decrease of both the rate and the molecular weight with increasing temperature, which is the feature of polymerisation reactions in which depropagation is occurring to an appreciable extent, has not been observed in this system. This was an unexpected result, since at the monomer concentrations (~1M) used, the ceiling temperature for high-polymer formation would have been expected to be about room temperature. However, Jessup's data show that $\Delta H^{\circ}_{\mathrm{lc}}$ for α-methylstyrene polymerisation increases markedly with decreasing chain length of the polymer when this is less than 10. Accordingly, the ceiling temperatures for pentamer, trimer, and dimer (the principal products in these experiments) are likely to increase in the order given, and all to be above room temperature. Depropagation, *i.e.*, reversal of the reaction given in equation (4), will therefore be unimportant in these experiments for values of $j < 6$. The proton-expulsion reaction (5) is thus the most important factor determining the overall rate and degree of polymerisation.

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