112. *The Kinetics of Catalytic Polymerizations. Part II.* The Mechanism of the Polymerization of Styrene catalyzed by Aluminium Chloride.*

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The kinetics of the individual stages of the aluminium chloride-catalyzed polymerization of styrene are considered on the basis of the experimental results given in Part I (preceding paper). Tentative conclusions are drawn concerning the mechanism of the reaction and in particular concerning the part played by the aluminium chloride in the reaction.

IN Part I * it has been shown that the initial rate of the polymerization of styrene in carbon tetrachloride solution catalyzed by aluminium chloride may be represented by the law

$$-\mathrm{d}M/\mathrm{d}t = kM_0B_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where M_0 and B_0 are the initial concentrations of styrene and aluminium chloride respectively. From this equation a reaction scheme may be built up taking into consideration the following possible initiation, propagation, chain-transfer, and chain-termination reactions (see, *e.g.*, Hulbert, Harman, Tobolsky, and Eyring, *Ann. New York Acad. Sci.*, 1943, **44**, 371).

Initiation.—This must take place by collisions of molecules of monomer (m) and of catalyst (b) :

$$\mathrm{m} + \mathrm{b} \longrightarrow \mathrm{m}_1^* \quad V_\mathrm{i} = k_\mathrm{i}MB \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In view of the fact that the course of the reaction is not influenced by co-catalysts, this becomes the only possible initiation reaction.

Propagation.—It is generally assumed that this occurs by the reaction

$$\mathrm{m}_1^* + \mathrm{m} \longrightarrow \mathrm{m}_2^* \quad V_\mathrm{p} = k_\mathrm{p}GM \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or, in general,

$$\mathrm{m}_n^* + \mathrm{m} \longrightarrow \mathrm{m}_{n+1}^*$$

where G is the concentration of the growing polymer chains.

Termination.—The only reaction compatible with (1) is of the type termed monomer deactivation :

$$\mathrm{m}_n^* + \mathrm{m} \longrightarrow \mathrm{m}_{n+1} \quad V_\mathrm{t} = k_\mathrm{t}\mathrm{GM} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This termination reaction has been suggested previously by Schultz (*Z. physikal. Chem.*, 1935, *B*, **30**, 379) for the thermal polymerization of styrene, but differs from that suggested by Eley and Pepper (*Trans. Faraday Soc.*, 1947, **43**, 112), Pepper (*ibid.*, 1949, **45**, 404), and Eley and Richards (*ibid.*, p. 436) for similar systems, who found that the reaction

$$\mathrm{m}_n^* \longrightarrow \mathrm{m}_n + \mathrm{b} \quad V_\mathrm{t}' = k_\mathrm{t}'G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

was necessary to satisfy their rate equation

$$-\mathrm{d}M/\mathrm{d}t = kM_0^2B_0$$

The monomer deactivation form of termination, (4), is in agreement however, with George and Wechsler's conclusion (*J. Polymer Sci.*, 1951, **6**, 725) that the termination reaction in the stannic chloride-catalyzed polymerization of styrene cannot be unimolecular. Furthermore, the unimolecular process, (5), would probably bring about the re-formation of active catalyst, which is contrary to our findings (see Part I).

* Part I, preceding paper.

Other possible termination reactions which have been shown to occur in free-radical polymerizations are :

$$\text{recombination} \quad \text{m}_n^* + \text{m}_m^* \longrightarrow \text{m}_{n+m}$$

$$\text{disproportionation} \quad \text{m}_n^* + \text{m}_m^* \longrightarrow \text{m}_n + \text{m}_m$$

These termination reactions have not been found to satisfy the conditions of the catalyzed reactions of the type considered here.

Transfer Reactions.—Solvent- and monomer-transfer reactions are the only transfer reactions which need be considered for the initial mechanism. These are :

$$\text{m}_n^* + \text{m} \longrightarrow \text{m}_n + \text{m}^* \quad V_{\text{tr}} = k_{\text{tr}}GM \quad \dots\dots \quad (6)$$

$$\text{m}_n^* + \text{s} \longrightarrow \text{m}_n + \text{s}^* \quad V_{\text{st}} = k_{\text{st}}GS \quad \dots\dots \quad (7)$$

possibly followed by

$$\text{s}^* + \text{m} \longrightarrow \text{m}^* + \text{s} \quad V_{\text{s}} = k_{\text{s}}S^*M \quad \dots\dots \quad (8)$$

where S and S^* are the concentrations of solvent and activated solvent molecules respectively.

Reactions involving deactivated polymer chains are unlikely to influence the kinetics of the initial reaction, but it must be borne in mind that conclusions derived from reactions proceeding to a high degree of polymerization may be influenced, in the later stages, by such reactions. This applies in particular to observations based on the molecular weight of the polymers formed.

The observation that one catalyst molecule initiates only one polymer chain on average (see Part I, Table 2) indicates that transfer reactions are of little importance in determining the mechanism of this particular polymerization, in contrast to Eley and Richards's conclusions (*Research*, 1949, **2**, 147; and *loc. cit.*). It therefore follows (see Mayo, *J. Amer. Chem. Soc.*, 1945, **65**, 2324; Breitenbach and Maschin, *Z. physikal. Chem.*, 1940, *A*, **187**, 175) that if the solvent participates in the reaction it does so by a true termination reaction, of the type given by (7) above.

The Kinetic Equation.—The assumption of the steady-state criterion,

$$\mathrm{d}G/\mathrm{d}t = 0 \quad \dots\dots \quad (9)$$

and hence that

$$V_{\text{i}} = V_{\text{t}} + V_{\text{st}} \quad \dots\dots \quad (10)$$

appears to be justified in this reaction. From equations (2), (4), (7), and (9), the concentration (G) of growing polymer chains may be calculated :

$$G = k_{\text{i}}MB/(k_{\text{t}}M + k_{\text{st}}S) \quad \dots\dots \quad (11)$$

The total rate of monomer consumption is given by :

$$-\mathrm{d}M/\mathrm{d}t = V_{\text{i}} + V_{\text{p}} + V_{\text{t}} + V_{\text{tr}} + V_{\text{s}}$$

in which we may with justification neglect V_{tr} and V_{s}.

Hence

$$-\mathrm{d}M/\mathrm{d}t = k_{\text{i}}MB[1 + M(k_{\text{p}} + k_{\text{t}})/(k_{\text{t}}M + k_{\text{st}}S)] \quad \dots \quad (12)$$

This is only in agreement with the experimental equation (1) if V_{st} is small compared with V_{t}, in which case equation (12) reduces to :

$$-\mathrm{d}M/\mathrm{d}t = k_{\text{i}}MB[2 + k_{\text{p}}/k_{\text{t}}] \quad \dots\dots \quad (13)$$

The decrease in molecular weight observed during the reaction (see Part I, Fig. 6) may be regarded as evidence for the operation of the solvent termination reaction (7), since the concentration of solvent must increase during the reaction, *i.e.*, the volume of the system decreases (see Pepper, *loc. cit.*). The chain length (n) in monomer units is then given by :

$$n = V_{\text{p}}/(V_{\text{t}} + V_{\text{st}}) \quad \dots\dots \quad (14a)$$

whence

$$1/n = k_{\text{t}}/k_{\text{p}} + k_{\text{st}}S/k_{\text{p}}M \quad \dots\dots \quad (14b)$$

The linearity of the plot of molecular weight against monomer concentration at time of precipitation (Part I, Fig. 6) is of no special significance, since the polymer precipitated is the whole mass of polymer formed up to that time. A more valid correspondence should be obtained between the molecular weight of the polymer precipitated and the monomer concentration when half the amount of reaction up to that time has occurred [*i.e.*, $\frac{1}{2}(M_0 + M)$]. The plot of molecular weight against $\frac{1}{2}(M_0 + M)$ is shown in Fig. 1 and is not found to be linear. From equation (14), however, we should expect that the plot of $1/n$ against $S/\frac{1}{2}(M_0 + M)$ should be linear and that this is the case is shown in Fig. 2.

FIG. 1.

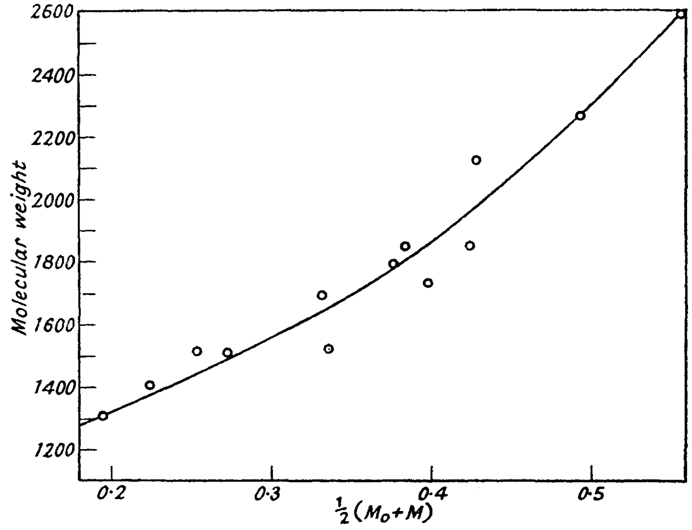
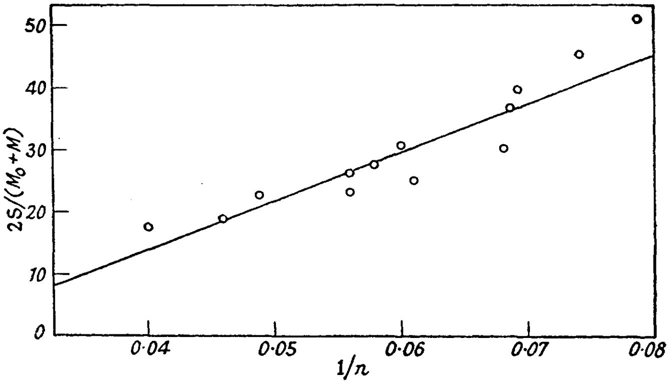


FIG. 2.



Calculation of Individual Reaction Constants.—From the slope of the line in Fig. 2 we may obtain the ratio k_{st}/k_p for which the value 0·0014 is found. The solvent termination reaction is thus clearly not responsible for the low molecular weight of the polymers formed and this can be attributed to the termination reaction (4). This fact, together with the unimportance of transfer reactions, enables us to write in place of (14*a*)

$$n \approx V_p/V_t$$

Since the average value of n is approximately 7 at 25°,

$$1/n = 0{\cdot}14 \approx k_t/k_p$$

Thus $k_t \approx 100k_{st}$, and this fact justifies to some extent the neglect of V_{st} in equation (12) for the range of initial concentrations studied, but indicates also that this value of k_{st}, derived as it is by a consideration of large amounts of reaction, is probably too high.

Putting the constant term of equation (13) equal to the experimental overall constant k of equation (1) we obtain

$$k = k_i(2 + k_p/k_t)$$

and, inserting the value of k_p/k_t (at 25° $k_p/k_t = 7$ and at 0° $k_p/k_t = 11$), we may calculate k_i at 0°, $k_i = 1{\cdot}1 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$, and, at 25°, $k_i = 1{\cdot}9 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$. Unfortunately these values cannot as yet be checked experimentally as no suitable inhibitor has been found for this reaction. Nevertheless, these values are of the order expected from a knowledge of the slower polymerization caused by stannic chloride as catalyst, for which Williams (*J.*, 1938, 1045) calculated a value of k_i of $1{\cdot}7 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ at 25° from a measurement of the inhibiting effect of hydrogen chloride on the reaction. The value of k_i at 25° for the corresponding free-radical reaction is $1{\cdot}32 \times 10^{-16}$ l. mole^{-1} sec.$^{-1}$ (Bamford and Dewar, *Proc. Roy. Soc.*, *A*, 1948, **192**, 309).

FIG. 3. *Variation of* $[\eta]$ *with temperature of preparation for poly-α-methyl styrene* (○) (*results of Hersberger, Reid, and Heiligmann*) *and polystyrene* (●).

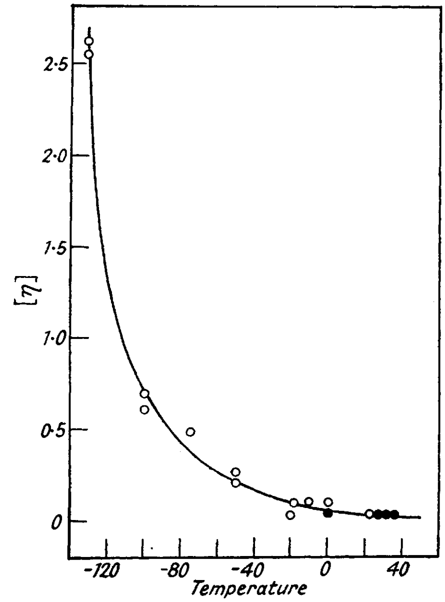
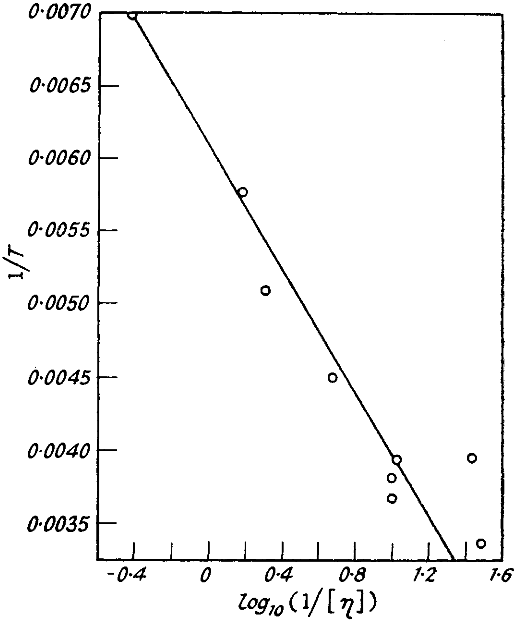


FIG. 4.



The extrapolation of the straight line in Fig. 2 from the values in dilute solution to give k_t/k_p is not justifiable (Hulburt, Harman, Tobolsky, and Eyring, *loc. cit.*).

Estimation of the Activation Energies.—From the variation of the molecular weight of the polymers with temperature of preparation it is possible to calculate $E_p - E_t - E_{st}$ (where E_p, E_t, and E_{st} are respectively the energies of activation for the propagation, termination, and solvent termination reactions). Introducing activation energies into equation (14*b*) and taking logarithms, we obtain :

$$\log \frac{1}{[\eta]} \propto \log \frac{1}{n} = \text{const.} + \frac{E_p - E_t - E_{st}}{\boldsymbol{R}T} + \log \frac{S}{M} \quad . \quad . \quad . \quad (15)$$

We may regard S/M as a constant if the reactions have the same initial monomer concentration. It then follows that a plot of log $(1/[\eta])$ against $1/T$ should give a straight line of slope $(E_p - E_t - E_{st})/\boldsymbol{R}$.

The variation of the polymer molecular weight with temperature for the aluminium chloride-catalyzed polymerization of styrene over the range 0° to 35° was too small to test this equation. However, Hersberger, Reid, and Heiligmann (*Ind. Eng. Chem.*, 1945, **37**,

1073) have investigated the variation of molecular weight with temperature over the range −130° to 23° of poly-α-methylstyrene, prepared with aluminium chloride as catalyst in ethyl chloride solution. At temperatures higher than −20° they also find only a small variation of molecular weight with temperature. Below this temperature, however, the molecular weight increases considerably as the temperature is lowered. Both sets of results are shown in Fig. 3, in which $[\eta]$ is plotted as a function of T. The two sets of results fall on the same curve where the temperatures are comparable. These data are applied to equation (15) in Fig. 4 which shows the required linear relation; from the slope, a value of −3800 cal./mole is obtained for $E_p - E_t - E_{st}$ on employing the relation between $[\eta]$ and the molecular weight given in Part I (*loc. cit.*). This value is close to that obtained by Eley and Richards (*loc. cit.*) for $(E_p - E_t)$ in the stannic chloride-catalyzed polymerization of octyl vinyl ether, −3300 cal./mole.

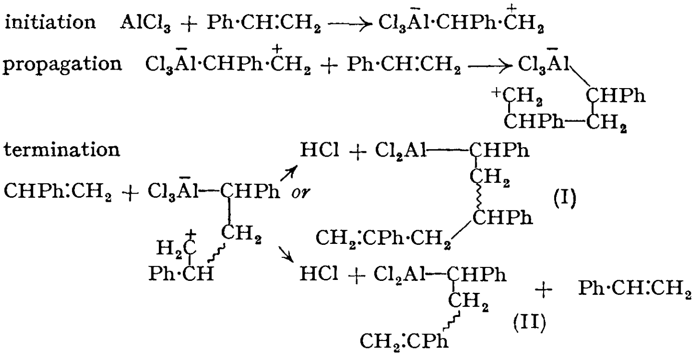
If we assume, in view of the agreement between the two sets of results in Fig. 3, that this value also holds for the same stage in the aluminium chloride-catalyzed polymerization of styrene, then since $E = E_i + E_p - E_t - E_{st}$, where E is the overall energy of activation and E_i that for the initiation reaction and E = 1200 cal./mole (Part I, *loc. cit.*), it follows that E_i = 5000 cal./mole. The value of k_i obtained above would thus not appear to be attributable to a high energy of activation.

The Reaction Mechanism.—The absence of any co-catalyst in the reaction excludes the carbonium-ion theory of Polanyi and Skinner (*J.*, 1947, 257) and Plesch and Polanyi (*ibid.*, p. 252) for which the presence of a co-catalyst containing hydrogen is essential. A possible alternative mechanism might be based on catalyst interaction with the solvent (Pepper, *loc. cit.*), *viz.*:

$$\text{initiation}\quad \mathrm{AlCl_3 + CCl_4 \longrightarrow AlCl_4^-\ CCl_3^+}$$
$$\text{propagation}\quad \mathrm{CCl_3^+ + Ph{\cdot}CH{:}CH_2 \longrightarrow Cl_3C{\cdot}CHPh{\cdot}CH_2^+}$$
$$\text{termination}\quad \mathrm{Cl_3C{\cdot}CHPh{\cdot}CH_2\ .\ .\ .\ Ph{\cdot}CH{\cdot}CH_2^+ + AlCl_4^- \longrightarrow Ph{\cdot}CH_2{\cdot}CH_2\ .\ .\ .\ CPh{:}CH_2 + AlCl_3 + CCl_4}$$

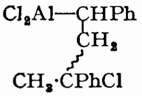
The objections to a scheme of this kind are so strong, however, that it must also be rejected. First, the catalyst is regenerated in an active form, and, secondly, the anion $AlCl_4^-$ should be capable of initiating polymerization in monomers with double bonds of electron-deficient character, *e.g.*, methyl methacrylate. We have found that aluminium chloride will not catalyze the polymerization of methyl methacrylate in carbon tetrachloride solution (see also Mayo and Lewis, *J. Amer. Chem. Soc.*, 1944, **66**, 1594). Also, this scheme leads to a kinetic expression for $-dM/dt$ which is not in agreement with equation (1), and to the presence of a double bond in each polymer molecule, which is contrary to our findings.

A reaction mechanism which is in agreement with all our results can, however, be based on the polarization of the monomeric double bond by the electrophilic catalyst, as already suggested by Price ("Reactions at Carbon–Carbon Double Bonds," Interscience Publ. Inc., 1946), *viz.*:



Subsequently, (I) and (II), which differ only in the degree of polymerisation, combine with hydrogen chloride, to give (III).

This mechanism satisfactorily explains (i) that catalyst is not regenerated in an active form, and (ii) that most of the polymer molecules do not contain an olefinic double bond. The presence of such a double bond in a small percentage of the molecules can be explained by the occasional non-recombination of the hydrogen chloride with the polymer. π-Complexes between Lewis acids and molecules containing conjugated systems are well known (see, *e.g.*, Dilke, Eley, and Perry, *Research*, 1949, **2**, 538). The objection raised by Plesch (*ibid.*, p. 267) to this type of mechanism, on the basis of the improbability of considerable charge separation in media of low dielectric constant, is over-ruled, since models of the polymers show that the ends of the chain can always readily take up a position of close proximity.



$$\begin{array}{l} Cl_2Al-CHPh \\ \qquad CH_2 \\ CH_2\cdot CPhCl \end{array}$$

(III)

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