440. *The Kinetics of Catalytic Polymerizations. Part III.* The Kinetics and Mechanism of the Polymerization of α-Methylstyrene catalyzed by Aluminium Chloride.*

By D. O. Jordan and A. R. Mathieson.

The initial rate of the aluminium chloride-catalyzed polymerization of α-methylstyrene in carbon tetrachloride and ethyl chloride solutions has been found to be proportional to the first power of the concentration of both α-methylstyrene and aluminium chloride. In carbon tetrachloride solution one catalyst molecule can initiate on average two polymer chains. On the addition of further catalyst to a reaction which has ceased before all the monomer has polymerized further polymerization occurs.

The polymers formed in carbon tetrachloride solutions are of very low molecular weight (about 300), but the molecular weight of those obtained in ethyl chloride solution has a value of 10^4. An empirical relation between intrinsic viscosity and molecular weight has been obtained for the polymers of low molecular weight.

Conclusions are drawn regarding the mechanism of the reaction, and a quantitative comparison with the corresponding styrene polymerization is made.

The polymerization of α-methylstyrene takes place less readily than that of styrene, the thermal polymerization not occurring spontaneously. Powerful Friedel–Crafts catalysts, however, will produce polymers of low molecular weight at room temperature although few studies have been made. Staudinger and Breusch (*Ber.*, 1929, **62**, 442) have investigated the effect of stannic chloride, titanic chloride, boron trichloride, and "Florida earth" on the liquid monomer, and Hersberger, Reid, and Heiligmann (*Ind. Eng. Chem.*, 1945, **37**, 1073) have obtained accurate information on the influence of temperature on the molecular weight and the molecular-weight distribution for the aluminium chloride-catalyzed polymerization in ethyl chloride solution. The influence of the dielectric constant of the solvent on the rate of the stannic chloride-catalyzed polymerization and on the molecular weight of the polymer has been investigated by Pepper (*Nature*, 1946, **158**, 789) who found that log (initial rate) increased linearly with the dielectric constant.

In Parts I and II (*J.*, 1952, **611**, 621) the kinetics and mechanism of the aluminium chloride-catalyzed polymerization of styrene in carbon tetrachloride solution were established, and we now report a similar study for α-methylstyrene. Measurements have also been made in ethyl chloride solution at 0° for correlation with the results obtained by Hersberger, Reid, and Heiligmann (*loc. cit.*).

Results and Discussion of the Reaction in Carbon Tetrachloride Solution.—Typical curves showing the course of the reaction at 25° are shown in Fig. 1. No induction periods have been observed.

Table 1. *The consumption of aluminium chloride during the polymerization of α-methylstyrene at 25°.*

Initial concn. of monomer (mole/l.)	Extent of polymerization (%)	Monomer consumed (x) (mole/l.)	Concn. of $AlCl_3$ (B_0) (mole/l.)	x/B_0	Chain length in monomer units
0·402	93	0·375	0·0707	5·3	2·25
0·321	83	0·266	0·0492	5·4	(1·87)
0·321	64	0·206	0·0380	5·4	2·71
0·451	58	0·261	0·0483	5·4	2·56

The function of the aluminium chloride in the reaction. As was observed for the polymerization of styrene (Part I, *loc. cit.*), when the catalyst was in relatively low concentration the reaction ceased before all the monomer had been converted, the ratio of monomer converted to aluminium chloride being a constant for such reactions, as shown

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* Part II, *J.*, 1952, 621.

in Table 1. On the addition of fresh catalyst to such reaction mixtures, further polymerization occurred (Fig. 2).

The molecular weight of the polymer. The molecular weights of the polymers formed were determined cryoscopically in benzene solution, care being taken to remove all entrained monomer from the polymer in view of the low molecular weight of the latter. This method gives a true value of the number average molecular weight since the solutions were found to obey Raoult's law. The empirical relation between the cryoscopic molecular weight and the intrinsic viscosity was found to be

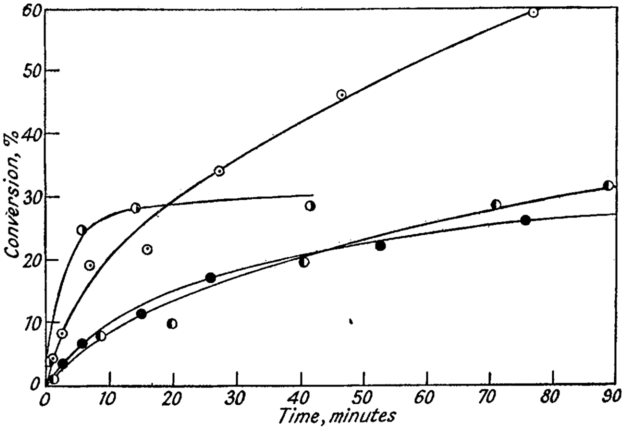
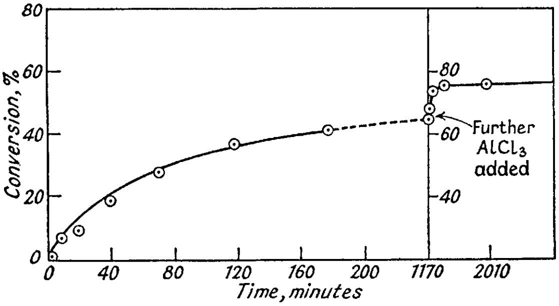


FIG. 1. *The course of polymerization in carbon tetrachloride solution at 25° (typical curves).*

$$[\eta] = 0{\cdot}0115 + 1{\cdot}93 \times 10^{-5}M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $[\eta] = \lim_{c \to 0} \eta_{sp}/c$ in which c is the concentration in g./100 c.c. of solution. This equation is similar to that obtained for styrene polymers (Part I, *loc. cit.*), but has been established over a much smaller range of molecular weight.

FIG. 2.



The Constitution of the Polymer.—For three different polymers of molecular weight 320, 221, and 267 the number of polymer molecules per olefinic double bond is 9·5, 13, and 68, respectively. It is therefore clear, despite the scatter of these values, that most of the polymer molecules do not contain an olefinic double bond.

Kinetic analysis of the rate curves. The initial rate of polymerization is found to be proportional to the first power of both the initial monomer (M_0) and catalyst (B_0) concentrations (Fig. 3), *viz.*:

$$-\mathrm{d}M/\mathrm{d}t = kM_0B_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the agreement between this relationship and the results being such as to exclude all relationships containing higher powers of M_0. The value of k at 25° is

$0{\cdot}92 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. This relationship has been confirmed by analysing the rate curves up to high degrees of polymerization, and equation (3) is then obeyed

$$-\mathrm{d}M/\mathrm{d}t = k'(M_0 - x)(B_0 - x/n') \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which x is the amount of monomer consumed in time t, and n' is the number of monomer molecules consumed per catalyst molecule ($n' = 5{\cdot}4$; see Table 1). As with styrene (Part I, *loc. cit.*) values of k' varied somewhat from one reaction to another because of the sensitivity of k' (but not of k) to the factor $(M_0 - n'B_0)$ which occurs in the denominator of the integrated form of equation (3).

The Reaction Mechanism.—The effect of water on the polymerization has not been specifically studied, but the marked similarity of the course of the polymerization of α-methylstyrene to that of styrene, together with the initiation of further polymerization on the addition of fresh catalyst to a reaction which has stopped, strongly suggests that, as for styrene, water is not an essential co-catalyst. Furthermore the good reproducibility of the reaction rate substantiates this view. We therefore consider that initiation proceeds by collisions between monomer (m) and catalyst (b) molecules, *viz.* :

FIG. 3. *The concentration dependence of the initial rate of polymerization at* 25°.

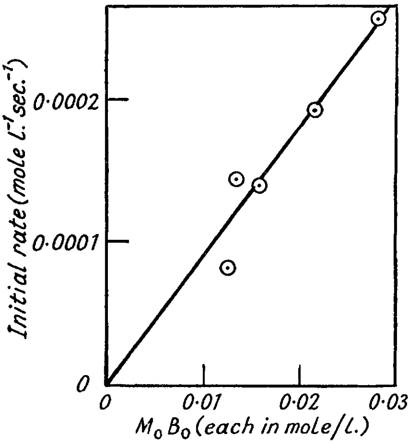
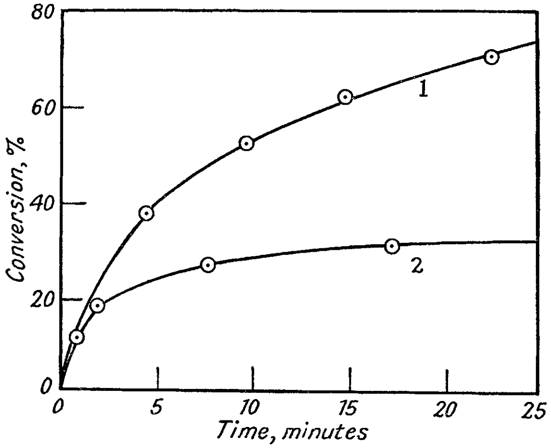


FIG. 4. *The course of polymerization in ethyl chloride solution at* 0° ($B_0 = 0{\cdot}00259$M; *curve* 1, $M_0 = 0{\cdot}755$M; *curve* 2, $M_0 = 0{\cdot}358$M.).



$$\mathrm{m} + \mathrm{b} \longrightarrow \mathrm{m}_1{}^* \qquad V_\mathrm{i} = k_\mathrm{i}MB \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Propagation then proceeds by the reaction

$$\mathrm{m}_1{}^* + \mathrm{m} \longrightarrow \mathrm{m}_2{}^* \qquad V_\mathrm{p} = k_\mathrm{p}GM \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where G is the concentration of the growing polymer chains. The only termination reaction compatible with equations (2) and (3) is monomer deactivation (see Part II, *loc. cit.*)

$$\mathrm{m}_n{}^* + \mathrm{m} \longrightarrow \mathrm{m}_{n+1} \qquad V_\mathrm{t} = k_\mathrm{t}GM \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The detailed mechanisms for the reactions will then be analogous to those already given for styrene (Part II, *loc. cit.*). From Table 1 it is evident that the ratio x/B_0, which represents the number of monomer molecules converted per molecule of catalyst, is twice the chain length of the polymer. This must indicate that each catalyst molecule produces two molecules of polymer and not one as in the case of styrene (Part I, *loc. cit.*), and it necessarily follows that a transfer mechanism is operating. Whether this transfer mechanism is monomer or solvent transfer is not clearly indicated from the experimental results. The method adopted for styrene (Part I, *loc. cit.*), in which the variation of the molecular weight during the course of the reaction was measured, could not be used here owing to the very small average molecular size of the polymer (two or three monomer units). However there is presumptive evidence in favour of solvent transfer. First, the solvent has been shown to participate in the polymerization of styrene (Part I, *loc. cit.*) and secondly monomer transfer does not occur for the aluminium chloride-catalyzed polymerization of α-methylstyrene in ethyl chloride solution at low temperatures (see Part V, *J.*, 1952, 2363). We therefore regard the transfer mechanism as being :

$$\mathrm{m}_n^* + \mathrm{s} \longrightarrow \mathrm{m}_n + \mathrm{s}^* \qquad V_{\mathrm{st}} = k_{\mathrm{st}}GS \quad . \; . \; . \; . \; . \; . \quad (7)$$

followed by

$$\mathrm{s}^* + \mathrm{m} \longrightarrow \mathrm{m}^* + \mathrm{s}$$

where S is the concentration of solvent.

Since the molecular fraction (monomer consumed)/(aluminium chloride concentration) [$= x/B_0$ (Table 1)] is approximately double the averate chain length, n, the rate of transfer must be approximately the same as the rate of termination. This follows since $V_{\mathrm{p}}/V_{\mathrm{t}} = x/B_0 = 5{\cdot}4$ and $V_{\mathrm{p}}/(V_{\mathrm{t}} + V_{\mathrm{st}}) = n = 2{\cdot}5$ (see Table 1); combination of these equations gives $V_{\mathrm{st}} = 1{\cdot}16V_{\mathrm{t}}$.

The concentration (G) of growing polymer chains may be obtained by applying the steady state criterion that $\mathrm{d}G/\mathrm{d}t = 0$ and $V_{\mathrm{i}} = V_{\mathrm{t}}$. It then follows that

$$G = k_{\mathrm{i}}B/k_{\mathrm{t}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

The total rate of monomer consumption is obtained from equations (4), (5), and (6),

$$-\mathrm{d}M/\mathrm{d}t = V_{\mathrm{i}} + V_{\mathrm{p}} + V_{\mathrm{t}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

$$= k_{\mathrm{i}}MB[2 + k_{\mathrm{p}}/k_{\mathrm{t}}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10a)$$

Equation (10*a*) agrees with the experimental equation (2) if

$$k = k_{\mathrm{i}}[2 + k_{\mathrm{p}}/k_{\mathrm{t}}] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

If the monomer deactivation reaction (6) follows the alternative possible course :

$$\mathrm{m}_n^* + \mathrm{m} \longrightarrow \mathrm{m}_n + \mathrm{m}$$

V_{t} must be deleted from equation (9) and equation (10*a*) becomes

$$-\mathrm{d}M/\mathrm{d}t = k_{\mathrm{i}}MB[1 + k_{\mathrm{p}}/k_{\mathrm{t}}] \quad . \; . \; . \; . \; . \; . \; . \quad (10b)$$

The distinction between equations (10*a*) and (10*b*) only becomes important when $k_{\mathrm{p}}/k_{\mathrm{t}}$ is relatively small as in the present case.

Calculation of reaction constants. From equations (5) and (6) $k_{\mathrm{p}}/k_{\mathrm{t}} = V_{\mathrm{p}}/V_{\mathrm{t}} = 5{\cdot}4$. By substituting this value for $k_{\mathrm{p}}/k_{\mathrm{t}}$ and the value for k obtained experimentally, and given above, into equation (11) we obtain $k_{\mathrm{i}} = 1{\cdot}2 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$.

An estimate may also be obtained of the values of the ratios $k_{\mathrm{st}}/k_{\mathrm{t}}$ and $k_{\mathrm{st}}/k_{\mathrm{p}}$ since $S \simeq 10$ and the average value of M (over the whole of the reaction) is 0·2; inserting these values in the equation

$$k_{\mathrm{st}}S/k_{\mathrm{t}}M = V_{\mathrm{st}}/V_{\mathrm{t}} = 1{\cdot}16$$

we obtain $k_{\mathrm{st}}/k_{\mathrm{t}} = 2 \times 10^{-2}$ and hence $k_{\mathrm{st}}/k_{\mathrm{p}} = 4 \times 10^{-3}$.

Comparison of the styrene and α-methylstyrene polymerizations. The overall and individual velocity constants are compared in Table 2. The main effects of the substitution are to decrease the overall rate and the rate of initiation and to increase the relative importance of transfer and termination reactions over the propagation reaction.

TABLE 2. *Comparison of the styrene and α-methylstyrene aluminium chloride-catalyzed polymerizations in carbon tetrachloride solution.*

	Styrene at 0°	Styrene at 25°	α-Methylstyrene at 25°
k (in l. mole^{-1} sec.$^{-1}$)	$1{\cdot}40 \times 10^{-2}$	$1{\cdot}68 \times 10^{-2}$	$0{\cdot}92 \times 10^{-2}$
k_{i} (in l. mole^{-1} sec.$^{-1}$) ...	$1{\cdot}1 \times 10^{-3}$	$1{\cdot}9 \times 10^{-3}$	$1{\cdot}2 \times 10^{-3}$
$k_{\mathrm{p}}/k_{\mathrm{t}}$	11	7·1	5·4
$k_{\mathrm{st}}/k_{\mathrm{p}}$	$1{\cdot}4 \times 10^{-3}$	—	4×10^{-3}
$k_{\mathrm{st}}/k_{\mathrm{t}}$	$1{\cdot}5 \times 10^{-2}$	—	2×10^{-2}
n	11	7	2·5

Results and Discussion of the Reaction in Ethyl Chloride Solution.—The reaction, which was carried out at 0°, was extremely rapid. The results, shown in Fig. 4, are adequately described by equations (2) and (3), and the mechanism is therefore the same as in carbon tetrachloride solution. The value of k at 0° is 0·61 l. mole^{-1} sec.$^{-1}$. This very great increase in reaction rate is in agreement with previous conclusions concerning the effect of dielectric constant on the rate of polymerization (Pepper, *loc. cit.*; George and Wechsler, *J. Polymer. Sci.*, 1951, **6**, 725).

The molecular weights of the polymer obtained were of the order of 10^4.

EXPERIMENTAL

The methods used in the measurement of reaction rates, molecular weights, viscosities, and degree of unsaturation, and in the precipitation of the polymer were as described in Part I (*loc. cit.*).

α-Methylstyrene was purified by repeated vacuum distillation. Ethyl chloride was of B.P. quality. The carbon tetrachloride and aluminium chloride were purified as described in Part I (*loc. cit.*).

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