695. *The Kinetics of Catalytic Polymerisations. Part XI.* Polymerisation of α-Methylstyrene catalysed by the Chloroacetic Acids.*

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Kinetics of the ionic polymerisation of α-methylstyrene catalysed by mono-, di-, and tri-chloroacetic acids have been investigated. The dependence of the initial rates on initial monomer ($[M]_0$) and catalyst ($[C]_0$) concentrations is $-d[M]_0/dt = k_0[M]_0^2[C]_0^{3\cdot2}$ and $-d[C]_0/dt = k_0'[C]_0$ for reactions in the absence of solvent, $-d[M]_0/dt = k_0[M]_0^2[C]_0^2$ and $-d[C]_0/dt = k_0'[M]_0^2[C]_0^2$ for ethylene dichloride solutions, and $-d[M]_0/dt = k_0[M]_0^2[C]_0$ for nitromethane solutions. After the initial stage in absence of solvent the kinetic order changes and becomes unity with respect to [M]. The acid catalysts are rapidly consumed initially, then more slowly, and finally may be regenerated. The rates of polymerisation are between 6 and 1960 times greater than for styrene and the effectiveness of the catalysts is related to their acid strengths. Reaction rate and overall activation energy increase with the dielectric constant of the medium, but the polymer molecular weight is only slightly changed. Polymers formed at room temperature are of low molecular weight, chiefly dimer and trimer; some of these are unsaturated, and the remainder and the higher polymer carry terminal chloroacetate groups, as shown by chemical and infrared analysis. The molecular weight increases at high values of $[C]_0$ and lower reaction temperatures; its distribution does not change during the reaction.

The kinetics and mechanism of the polymerisation of styrene catalysed by the chloroacetic acids have already been studied;[1,2,3] the results of a similar study of α-methylstyrene are reported here. In general, as with catalysis by chloroacetic acids,[4] α-methylstyrene is cationically polymerised more rapidly than styrene, but forms polymers of only very low molecular weight at room temperature.[5] A detailed comparison of the two monomers in these systems should help to elucidate the special behaviour of α-methylstyrene towards polymerisation. As for styrene, the reaction rates are very sensitive to reactant concentrations and high acid concentrations must be employed to obtain measurable rates.

Recent studies of the polymerisation of α-methylstyrene by metal halide catalysts [6,7,8] have shown that the rate is proportional to $[M]^x[C]$, where x can have values from 1 to 2 depending on reaction conditions. The polymers may be largely unsaturated,[8] or saturated,[7] and have substituted phenylindane end groups.[6] The polymer molecular weights are proportional to [M].[6,8] α-Methylstyrene will not polymerise [9,10] ionically

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* Part X, *J.*, 1957, 3631.

[1] Brown and Mathieson, *J.*, 1957, 3612.

[2] Brown and Mathieson, *J.*, 1957, 3620.

[3] Brown and Mathieson, *J.*, 1957, 3631.

[4] Pepper, *Quart. Rev.*, 1954, **8**, 88.

[5] Brown and Mathieson, *J.*, 1957, 3608.

[6] Dainton and Tomlinson, *J.*, 1953, 151.

[7] Jordan and Mathieson, *J.*, 1952, 2354.

[8] Worsfold and Bywater, *J. Amer. Chem. Soc.*, 1957, **79**, 4917.

[9] Dainton and Ivin, *Nature*, 1948, **162**, 705; *Trans. Faraday Soc.*, 1950, **46**, 331.

[10] McCormick, *J. Polymer Sci.*, 1957, **25**, 488.

above 61° and has a low heat of polymerisation.[10,11] This led Dainton and Ivin [9] to suggest that depropagation was important but Worsfold and Bywater [8] concluded that it is not significant for the formation of short chains. Steric hindrance to polymerisation has been suggested [12] to explain low molecular weights and heat of polymerisation, but very high polymers can be made at low temperatures.[13] Decreased importance of transfer relative to termination at low temperatures has been suggested to explain this.[14]

RESULTS AND DISCUSSION

General Features of the Reactions.—The polymerisations, studied in ethyl bromide, ethylene dichloride, and nitromethane, and in the absence of solvent, are quantitative. At room temperature the main products (a sticky solid or viscous liquid) are dimer and trimer, even in nitromethane, but at higher catalyst concentrations some polymer of molecular weight 1000—1500, precipitated by methanol, is formed along with the methanol-soluble dimer–pentamer. The reaction rates are appreciably faster than for styrene and yellow-brown colours in the product are developed more rapidly, but are easily destroyed by washing with water to remove excess of acid. The reactions, more rapid in media of high dielectric constant, do not proceed in nitrobenzene, acetone, or alcohol, and are retarded by *p*-benzoquinone and 1 : 3 : 5-trinitrobenzene, presumably by the same mechanism as that established for styrene [1] since the same red colour appears and quinhydrone is precipitated. Monochloroacetic acid is an effective catalyst, in contrast to its inertness towards styrene, but acetic acid has no effect even in nitromethane. The rate of reaction is greater the greater the acid strength of the catalyst, but the molecular weight and composition of the product are similar for the three acids. The acid is rapidly consumed at first, the rate decreasing as reaction proceeds as for styrene, but the acid can be re-formed towards the end.

The methods used to follow the rates of consumption of monomer and acid need careful consideration before they can be related to the true rates of reaction. Measurements of acid concentration were based on extraction of residual free acid into water. Those of monomer concentration were based on direct bromination in the polymerising solution, so monomer and acid would not appear to be consumed by reversible formation of a monomer–acid complex. Also, a considerable fraction of the polymer formed at room temperature consists of unsaturated dimer and trimer which readily take up bromine, so it was necessary to separate the product quantitatively and measure its bromine uptake for each determination of monomer consumption during the reaction. The amount of product separated also checked the bromine titration method.

Molecular Weight and Composition of the Product.—A series of reactions was carried out with di- and tri-chloroacetic acids in which the product was quantitatively separated and its molecular weight ($\overline{M}_n$) measured (Table 1). The average molecular weight is only slightly greater for reactions in nitromethane than in the absence of solvent but at high catalyst concentrations it increases with catalyst concentration, more pronouncedly than for styrene. This can be represented approximately as

$$\overline{M}_n = 236 + 6[\mathrm{C}]_0^2$$

The effect of temperature on molecular weight was studied by using only ethyl bromide as solvent, since at −80° the rate in non-polar solvents such as *iso*pentane was too small to measure. The molecular weight is higher for reactions at low temperatures, and, as for the styrene–chloroacetic acid [1] and α-methylstyrene–aluminium chloride [14] systems, $\log (1/\overline{M}_n) \propto 1/T(^\circ\mathrm{K})$. At −80° the poly-α-methylstyrene formed has approximately

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[11] Roberts and Jessup, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 11.
[12] Evans and Polanyi, *Nature*, 1948, **152**, 738.
[13] Hersberger, Reid, and Heiligmann, *Ind. Eng. Chem.*, 1945, **37**, 1073.
[14] Jordan and Mathieson, *J.*, 1952, 2363.

the same molecular weight as polystyrene formed under the same conditions. Evidently the factors which limit molecular weight and produce large amounts of dimer at room temperature are not important at low temperatures.

TABLE 1. *Molecular weight of the polymer.*

A. *Effect of acid concentration* ($[C]_0$). (Dichloroacetic acid in nitromethane, 25°.)

$[C]_0$ (mole l.$^{-1}$), $\overline{M}_n$	3·1, 265	4·6, 330	6·3, 430	7·6, 550

B. *Effect of temperature.* (Trichloroacetic acid in ethyl bromide.)

Temp., $\overline{M}_n$	−80°, 2400	0°, 400	40°, 250

C. *Effect of extent of reaction.* (Trichloroacetic acid, no solvent, $[C]_0$ = 1·0 mole l.$^{-1}$, 25°.)

Monomer conversion (%)	18·3	29·6	54·3	71·8	89·9
$\overline{M}_n$	380	370	370	385	365

D. *Limiting viscosity number* ($[\eta]$). (In benzene, 25°.)

$[\eta]$	0·0080	0·012	0·017	0·0185	0·0190	0·0235	0·0245	0·0275
$\overline{M}_n$	270	330	460	500	560	600	690	770

E. *Effect of solvent.* (Dichloroacetic acid, $[C]_0$ = 1·0 mole l.$^{-1}$, 25°.)

Solvent, $\overline{M}_n$	None, 370	Nitromethane, 400

The limiting viscosity number–number-average molecular weight relationship is $[\eta] = 3{\cdot}50 \times 10^{-5}\overline{M}_n$ for unfractionated polymers prepared at normal temperatures, with concentration expressed as grams of polymer per 100 ml. of solution at 25°. These values of $[\eta]$ are somewhat greater that those for poly-α-methylstyrenes of comparable molecular weight prepared by other methods, perhaps owing to the chloroacetate end-groups.

TABLE 2. *Molecular-weight distribution.*

A. *At end of reaction.* (Trichloroacetic acid, 25°.) Weight % of polymer in various fractions given.

System:	(*a*) No solvent $[C]_0$ = 1·0			(*b*) $CH_3{\cdot}NO_2$ soln. $[C]_0$ = 1·0			(*c*) $CH_3{\cdot}NO_2$ soln. $[C]_0$ = 5·0		
Range of M_n	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
236—350	55·8	59·3	61·7	46·3	47·2	51·6	42·8	45·7	50·1
350—500	27·2	26·9	21·8	23·8	20·9	21·3	18·7	19·6	15·3
500—800	13·6	13·9	14·3	28·3	28·7	21·6	21·7	16·5	19·8
>800	0	0	0	0	0	0	17·3	16·1	15·6

B. *Effect of extent of reaction.* (Dichloroacetic acid, no solvent, $[C]_0$ = 1·0, 25°.)

Monomer conversion (%)	38·5	48·3	59·6	61·7	75·1	100
Fraction $\overline{M}_n$ = 236—350 as weight % of polymer	55·0	57·5	54·7	53·5	51·0	58·3

The molecular-weight distribution was measured for three systems at 25° with trichloroacetic acid, (*a*), (*b*), and (*c*) (Table 2). Three polymers were fractionated for each system. The highest fraction, which appeared only when the catalyst was in high concentration, was insoluble in methanol and had a molecular weight between 1000 and 1500. Reproducibility in the fractionation was reasonably good for the low-pressure distillation method used. There was no change in the molecular-weight distribution with extent of reaction.

Constitution and Stability of Polymers.—Polymers were microanalysed for carbon, hydrogen, and chlorine and examined for unsaturation by catalytic microhydrogenation (Table 3). Nos. 1, 2, and 3 are further fractions obtained by fractionating the 236—350 fraction. They have one double bond per molecule and no chloroacetate group. The fraction 236—350 is clearly a mixture of unsaturated dimer (236) and unsaturated trimer (354). Nos. 5 and 6 are the 350—500 fraction. They are fully saturated and contain one trichloroacetate group per molecule and are evidently dimer trichloroacetate (398) and some trimer trichloroacetate (516). Nos. 9—12 are unfractionated polymers of low molecular weight, showing how the proportion of unsaturated molecules falls as molecular weight rises. Nos. 7 and 8 are the >800 fraction and are fully saturated but contain less than one chloroacetate group per polymer molecule. Distillation of the esterified polymers at atmospheric pressure expels the chloroacetate group leaving a terminal double bond, as for polystyrene, and No. 4 is the 500—800 fraction which has been distilled.

Poly-α-methylstyrene prepared by chloroacetic acid catalysis consists of unsaturated dimer and trimer, dimer and trimer esters and higher esters, and perhaps some higher-molecular weight material which contains neither double bonds nor chloroacetate groups. From the molecular-weight distributions, the analyses of the polymers, and the average molecular weights of the fractions, the composition of the polymers is approximately as shown in Table 4. The composition is not significantly altered by change of acid, or by the use of ethylene dichloride as solvent, but nitromethane increases the proportion of higher esters, and high initial catalyst concentrations lead to the formation of some higher polymer.

TABLE 3. *Microanalysis of the polymers.*

No.	(M_n)		C (%)	H (%)	Cl (%)	No. of double bonds per molecule	No. of trichloroacetate groups per molecule
1	240	Fraction 236—500	91·1	8·6	0	0·97	0
2	245	,,	90·1	8·4	0·4	1·0	0·010
3	354	,,	89·2	8·2	0·9	1·0	0·031
4	472	Fraction 500—800, distilled	89·9	7·9	0	1·0	0
5	423	Fraction 350—500	59·5	5·2	24·6	0	0·98
6	450	,,	59·2	5·5	24·3	0	1·02
7	1200	Fraction >800	85·0	6·9	2·1	0	0·24
8	1560	,,	85·1	7·0	3·8	0	0·54
9	260	Unfractionated	—	—	—	1·13	—
10	280	,,	—	—	—	1·01	—
11	320	,,	—	—	—	0·67	—
12	360	,,	—	—	—	0·18	—

TABLE 4. *Approximate composition (weight %) of polymers formed at* 25°.

System	No solvent	$CH_3{\cdot}NO_2$ solution	$CH_3{\cdot}NO_2$ solution $[C]_0 = 5{\cdot}0$
Unsaturated dimer	47	37	37
Unsaturated trimer	12	9	9
Dimer ester	25	22	18
Trimer—pentamer ester	14	26	19
Higher polymer	0	0	16

The interpretation of chlorine content in terms of chloroacetate groups receives confirmation from the infrared spectra of the polymers (Table 5). Sample II was prepared by trichloroacetic acid catalysis in the absence of solvent. Sample III is a portion of sample II hydrolysed by refluxing it with potassium hydroxide in octyl alcohol to remove trichloroacetate groups. Sample I is thermal polystyrene for comparison. The spectrum of ethyl trichloroacetate was measured for comparison (Table 6), and comparison can also be made with the spectra of polystyrene prepared by trichloroacetic acid catalysis and of benzyl trichloroacetate.[2] The bands at 815 m, 1245 s, 1290 m, and 1760 s in sample II indicate that it contains combined trichloroacetate residues and these are reduced to 806 w, 1245 m, 1290 w, and 1760 w in the hydrolysed sample III. Bands at 720 and 1090 (sample II and III) could be due to *ortho*-disubstitution, and the 2870 band in sample I occurs in sample II but is absent from sample III. It could be due to $\equiv CH$ converted by the removal of a combined chloroacetate group into $>CH_2$. This suggests the occurrence of the substituted indane structure. The presence of a small amount of free trichloroacetic acid in sample II may be indicated by the band at 2520 m. Bands at 1795 and 3040 in samples II and III are due to $-CH{=}CH_2$ groups in the unsaturated dimer and trimer, and that at 1390 is due to the methyl groups.

Initial Rates of Polymerisation.—The rates of monomer consumption were measured at 25° with all three acids in the absence of solvent, and in ethylene dichloride and nitromethane solutions. Fig. 1 shows typical reaction–time curves, which were reproduced to about 2%. The sealed-tube method was used. The results are collected in Table 7, which shows the linear dependence of the initial rates on the appropriate powers of $[M]_0$ and $[C]_0$. The water concentration was within the range for which the rate was independent of water concentration for styrene. From the similarity of this polymerisation to that of styrene it is presumed that the rate in the absence of solvent depends on water concentration at low water concentrations, but this has not been experimentally demonstrated for α-methylstyrene. The kinetic orders are the same for all three acids in a given medium, and the initial rates are described by the equations

TABLE 5. *Infrared spectra of the polymers* (*cm.*$^{-1}$) (s, *absorption* $> 70\%$; m, 30—70%; w $< 30\%$).

Sample No.	I	II	III	I	II	III	I	II	III
	667m	—	—	1077m	1077m	1083m	—	1580m	1580m
	683s	683s	680s	—	1090w	1100m	1585m	1585s	1585s
	700s	690s	700s	1150m	1150m	1150m	1610s	1610w	—
	—	720m	720w	1175m	—	—	1680w	1670w	1670w
	760s	760s	760s	1185m	1185m	1180m	1730m	—	—
	—	780m	780m	1215w	—	—	—	1760s	1760w
	—	815m	806w	—	1245m	1245m	—	1795m	1795m
	850m	853m	840w	1285m	1290m	1290w	1810m	1825m	1830m
	—	890m	—	1295m	—	—	1860m	1875m	1880m
	910s	910m	900m	—	1315w	1315w	1930m	1905m	—
	930m	930m	—	1350m	1365m	1370m	—	2520m	—
	950m	965m	950m	—	1390m	1390m	2870m	2870m	—
	985m	—	—	1450m	1450m	1450m	2950s	2980s	2950m
	993m	1000m	1000w	1470m	1470m	1470m	—	3040s	3040m
	1015m	1015s	1030s	1485s	—	—	—	3140m	3140m
	1045m	1050m	—	—	1505s	1505s	3190m	3190m	3190m
	—	1057s	—	1545w	1550s	1550s	3220m	—	—

TABLE 6. *Infrared spectrum of ethyl trichloroacetate* (*cm.*$^{-1}$).

683w *	750w	828s *	960s	1100m *	1160s *	1229m *	1266m
1300s *	1370m	1393m	1445m	1470m	1760m *	2976m	—

* Characteristic of trichloroacetate group.)

$$-d[M]_0/dt = k_0[M]_0^2[C]_0 \text{ for nitromethane solutions}$$

$$-d[M]_0/dt = k_0[M]_0^2[C]_0^2 \text{ for ethylene dichloride solutions}$$

$$-d[M]_0/dt = k_0[M]_0^2[C]_0^{3\cdot2} \text{ in absence of solvent}$$

These kinetic orders are the same as for styrene,[1] except that 3·2 replaces 3·5 as exponent of $[C]_0$ in the last. The initial rates given in Table 7 were obtained from experiments in

TABLE 7. *Initial rates of polymerisation* (*mole l.*$^{-1}$ *min.*$^{-1}$) *at* 25°.

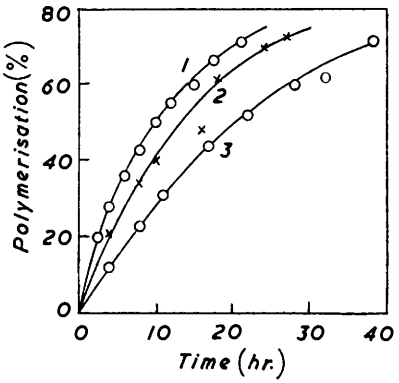
Medium	No solvent		Ethylene dichloride		Nitromethane.	
Acid	Initial rate	$[M]_0^2[C]_0^3$	Initial rate	$[M]_0^2[C]_0^2$	Initial rate	$[M]_0^2[C]_0$
$CH_2Cl\cdot CO_2H$	3·28 × 10^{-6}	210	3·43 × 10^{-8}	0·35	0·48 × 10^{-4}	3·6
	4·12 ,,	264	5·22 ,,	0·54	1·10 ,,	8·5
	4·75 ,,	303	7·28 ,,	0·75	1·65 ,,	12·1
	5·52 ,,	354	8·83 ,,	0·92	2·09 ,,	16·0
	6·80 ,,	430	11·1 ,,	1·13	2·52 ,,	19·4
$CHCl_2\cdot CO_2H$	3·0 × 10^{-3}	226	2·68 × 10^{-5}	0·24	0·042	3·2
	4·1 ,,	294	4·78 ,,	0·44	0·106	8·2
	4·7 ,,	340	6·22 ,,	0·58	0·152	11·8
	5·7 ,,	400	8·32 ,,	0·78	0·198	15·5
	6·8 ,,	475	11·6 ,,	1·06	0·258	20·2
$CCl_3\cdot CO_2H$ ...	2·43 × 10^{-2}	194	2·85 × 10^{-4}	0·26	0·28	2·6
	3·24 ,,	251	4·47 ,,	0·41	0·78	7·1
	4·05 ,,	311	6·75 ,,	0·60	1·22	11·3
	4·73 ,,	363	9·18 ,,	0·82	1·63	15·0
	6·23 ,,	454	12·2 ,,	0·99	2·04	18·8

which both $[M]_0$ and $[C]_0$ were varied. In addition, the exponent 3·2 was checked for di- and tri-chloroacetic acid catalysis by experiments with constant $[M]_0$, and $[C]_0$ varied by using ethylene dichloride and ethyl chloride as diluents for the two acids respectively so as not to alter the dielectric constant of the system. Plots of log $(-d[M]_0/dt)$ against log $[C]_0$ gave straight lines of slope 3·2. The values of the overall initial rate constants (k_0) are shown in Table 8, together with the corresponding values for styrene.[1] (The units of k^0 for styrene, not specified in ref. 1, are mole l.$^{-1}$ min.$^{-1}$.) Although α-methylstyrene is more rapidly polymerised than styrene in every case, the relative rate is different in each system, lying between 6·1 for trichloroacetic acid–ethylene dichloride and 1960 for the dichloro-acid with no solvent. For a particular solvent, the relative rate for dichloroacetic acid catalysis is always greater than for trichloroacetic acid catalysis and the ratio of the value of the function [k_0 (α-methylstyrene)/k_0(styrene)] with dichloroacetic to that with trichloroacetic acid is roughly constant, being 4·7, 5·7, and 5·3 for no solvent, ethylene dichloride solution, and nitromethane solution, respectively. The relative rate for a particular acid does not depend on the dielectric constant of the medium, being in the order no solvent $\gg$ nitromethane solutions $>$ ethylene dichloride solutions.

TABLE 8. *Overall initial rate constants at 25° (mole l.$^{-1}$ min.$^{-1}$).*

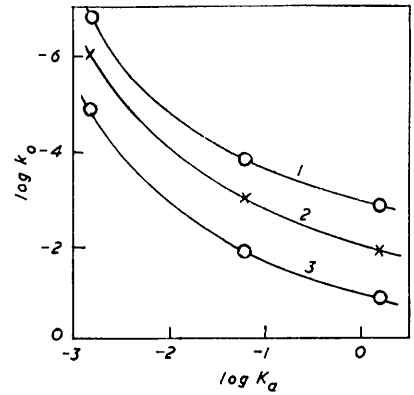
System	k_0 (α-methylstyrene)	k_0 (styrene)
$CCl_3\cdot CO_2H$–no solvent	$1{\cdot}30 \times 10^{-3}$	$3{\cdot}1 \times 10^{-6}$
$CHCl_2\cdot CO_2H$–no solvent	$1{\cdot}43 \times 10^{-4}$	$7{\cdot}3 \times 10^{-8}$
$CH_2Cl\cdot CO_2H$–no solvent	$1{\cdot}56 \times 10^{-7}$	0
$CCl_3\cdot CO_2H$–$C_2H_4Cl_2$	$1{\cdot}13 \times 10^{-2}$	$1{\cdot}85 \times 10^{-3}$
$CHCl_2\cdot CO_2H$–$C_2H_4Cl_2$	$1{\cdot}08 \times 10^{-3}$	$3{\cdot}12 \times 10^{-5}$
$CH_2Cl\cdot CO_2H$–$C_2H_4Cl_2$	$9{\cdot}7 \times 10^{-7}$	0
$CCl_3\cdot CO_2H$–$CH_3\cdot NO_2$	0·110	$7{\cdot}3 \times 10^{-3}$
$CHCl_2\cdot CO_2H$–$CH_3\cdot NO_2$	$1{\cdot}28 \times 10^{-2}$	$1{\cdot}6 \times 10^{-4}$
$CH_2Cl\cdot CO_2H$–$CH_3\cdot NO_2$	$1{\cdot}30 \times 10^{-5}$	0

FIG. 1. *Typical reaction–time curves for trichloroacetic acid catalysis in nitromethane solution (25°).*



1, $[C]_0$ = 0·50; 2, $[C]_0$ = 0·37; 3, $[C]_0$ = 0·25.

FIG. 2. *Catalytic activity and acid strength (25°).*



1, No solvent; 2, ethylene dichloride solution; 3, nitromethane solution.

Comparison of the Catalytic Activities of the Chloroacetic Acids.—The catalysts are more effective the greater their acid strengths, but the overall initial rate constants do not obey the relation $k_0 = GK_a^x$, where K_a is the acid dissociation constant and G and x are constants for a given reaction. Fig. 2 shows plots of log K_a against log k_0 for the three media, and the three curves are similar. The rate of an ionic polymerisation depends on other factors than the proton-donating power of the catalyst, but nevertheless k_0 and K_a

are related although the Brønsted relation cannot be expected to hold. If the polymerisation proceeds by a mechanism similar to that postulated for styrene,[3] as the kinetic orders suggest, it may be that the acid strength of the catalyst influences the reactivity of the monomer–catalyst complex in initiation and propagation.

Influence of Dielectric Constant and Temperature on the Polymerisation.—The rate is greater in media of higher dielectric constant (Tables 7 and 8), as for styrene,[1] and demonstrates the ionic character of the polymerisation. The overall initial rates of polymerisation were determined at 0°, 25°, and 40° for the three media. The Arrhenius equation is obeyed over this range of temperature and the overall energies of activation (E_0) are shown in Table 9. The value of E_0 increases with dielectric constant of the solvent, though the reactions in absence of solvent seem anomalous. The values for trichloroacetic acid are greater than for di- and mono-chloroacetic acid. In general, as for styrene,[1] the more rapid reactions have the higher values of E_0, interpreted for styrene in terms of monomer-acid complex formation.[3]

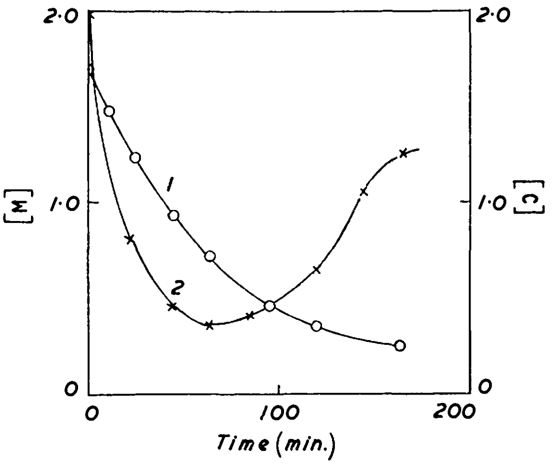


Fig. 3. *Consumption of monomer and acid during reaction for dichloroacetic acid catalysis in ethylene dichloride solution (25°).*

1, Monomer; 2, acid.

Table 9. *Overall energy of activation* (E_0) (*kcal. mole*$^{-1}$).

Medium	Dielectric constant	$CCl_3{\cdot}CO_2H$	$CHCl_2{\cdot}CO_2H$	$CH_2Cl{\cdot}CO_2H$
No solvent	—	14	6·5	4·0
$C_2H_4Cl_2$	10·5	8	6·0	6·5
$CH_3{\cdot}NO_2$	39	15	—	8·0

For the trichloroacetic acid–ethyl bromide system, log $(1/\bar{M}_n)$ is linear with $1/T$, and a value for E_n for $-4{\cdot}5$ kcal. mole^{-1} is obtained. This is normally identified as the difference between the energy of activation for chain propagation and chain breaking, and the value for α-methylstyrene is much greater than that for styrene[1] ($-0{\cdot}85$ kcal. mole^{-1}). This means that at low temperatures high-molecular weight poly-α-methylstyrene can be obtained.

Consumption of the Acid Catalysts.—The acids are consumed during polymerisation to a much larger extent that is to be expected from the incorporation of catalyst fragments in the polymer. Fig. 3 shows a typical acid-consumption curve. Initially the acid is consumed rapidly, but the proportionate consumption of acid falls as reaction proceeds and eventually actual regeneration of acid takes place. This behaviour is more extreme than that of styrene, for which the final regeneration of acid did not occur.[1] The initial rapid consumption of acid is best ascribed, as for styrene, to monomer–acid complex formation.

The consumption of acid at the beginning of the reaction is more marked for trichloroacetic acid. Table 10 shows the initial rates of catalyst consumption for four systems. For reactions in the absence of solvent

$$-\mathrm{d}[\mathrm{C}]_0/\mathrm{d}t = k_0'[\mathrm{C}]_0$$

$k_0' = 0{\cdot}060$ and $0{\cdot}015$ for trichloroacetic and dichloroacetic acids respectively. For ethylene dichloride solutions, the ratio $-\mathrm{d}[\mathrm{M}]_0/\mathrm{d}t/-\mathrm{d}[\mathrm{C}]_0/\mathrm{d}t$ is constant, approximately unity for trichloroacetic acid, and 2 for dichloroacetic acid catalysis. Hence, for ethylene dichloride solutions,

TABLE 10. *Initial rate of catalyst consumption (mole l.$^{-1}$ min.$^{-1}$, 25°).*

System	$[\mathrm{M}]_0$	$[\mathrm{C}]_0$	$-\mathrm{d}[\mathrm{M}]_0/\mathrm{d}t$	$-\mathrm{d}[\mathrm{C}]_0/\mathrm{d}t$	$\frac{-\mathrm{d}[\mathrm{C}]_0/\mathrm{d}t}{[\mathrm{C}]_0}$	$\frac{-\mathrm{d}[\mathrm{M}]_0/\mathrm{d}t}{-\mathrm{d}[\mathrm{C}]_0/\mathrm{d}t}$
$CCl_3{\cdot}CO_2H$–no solvent	4·40	1·41	0·217	0·094	0·067	—
	5·80	1·10	0·058	0·065	0·059	—
	6·50	0·47	0·0057	0·028	0·060	—
$CHCl_2{\cdot}CO_2H$–no solvent ...	5·20	3·50	0·165	0·050	0·0143	—
	6·00	1·97	0·0394	0·029	0·0147	—
	6·70	1·51	0·0222	0·028	0·0185	—
$CCl_3{\cdot}CO_2H$–$C_2H_4Cl_2$	1·66	1·41	0·0605	0·055	—	1·1
	2·18	0·87	0·0407	0·034	—	1·2
	3·00	0·55	0·0308	0·024	—	1·3
$CHCl_2{\cdot}CO_2H$–$C_2H_4Cl_2$	1·70	2·16	0·0142	0·0080	—	1·8
	2·70	1·61	0·0206	0·010	—	2·0
	2·90	0·86	0·0062	0·0030	—	2·1

$$-\mathrm{d}[\mathrm{C}]_0/\mathrm{d}t = k_0'[\mathrm{M}]_0^2[\mathrm{C}]_0^2$$

with $k_0' = 1{\cdot}1 \times 10^{-2}$ and $0{\cdot}5 \times 10^{-3}$ for trichloroacetic acid and dichloroacetic acid catalysis respectively.

This is a more extended study of the initial rate of acid consumption than was made for styrene.[3] It does not permit conclusions to be drawn concerning the stoicheiometric formulæ of the monomer–catalyst complexes, and so the formulæ suggested for them in the case of styrene[3] must be accepted with reserve. The high initial rates of acid consumption, the high kinetic orders with respect to acid, and the increase of activation energy with reaction rate still require the postulate of monomer–catalyst complex formation however. Acid concentration cannot be determined by titration for the nitromethane solutions.

Internal Order of Reaction Curves.—Some typical reactions were analysed to high degrees of conversion, and the "internal" kinetic orders obtained compared with the kinetic orders from the initial rates. The rate of reaction at 50% polymerisation ($-\mathrm{d}[\mathrm{M}]_{\frac{1}{2}}/\mathrm{d}t$) was determined and compared with that calculated from the kinetic order as determined by the initial rates. For the calculation only catalyst

TABLE 11. *Reaction rate at 50% polymerisation* (25°) *(mole l.$^{-1}$ sec.$^{-1}$).*

Medium	$10^4(-\mathrm{d}[\mathrm{M}]_0/\mathrm{d}t)$ (initial rate)	$10^4(-\mathrm{d}[\mathrm{M}]_{\frac{1}{2}}/\mathrm{d}t)$ (rate at 50% polymn.)	$\frac{-\mathrm{d}[\mathrm{M}]_{\frac{1}{2}}/\mathrm{d}t}{-\mathrm{d}[\mathrm{M}]_0/\mathrm{d}t}$ (found)	$\frac{-\mathrm{d}[\mathrm{M}]_{\frac{1}{2}}/\mathrm{d}t}{-\mathrm{d}[\mathrm{M}]_0/\mathrm{d}t}$ (calc.)
α-Methylstyrene–no solvent...	10·8	5·00	0·463	0·215
	0·217	0·108	0·498	0·215
	4·00	1·84	0·460	0·215
α-Methylstyrene–$CH_3{\cdot}NO_2$ ...	0·234	0·0683	0·292	0·240
	0·184	0·045	0·245	0·240
	0·817	0·217	0·266	0·240
Styrene–no solvent	2·67	1·05	0·393	0·215
	1·38	0·567	0·410	0·215
Styrene–$CH_3{\cdot}NO_2$	0·267	0·085	0·318	0·240
	0·484	0·128	0·265	0·240
	0·183	0·058	0·317	0·240

permanently removed from the reaction by combination into the polymer was regarded as consumed. The comparison was made for some of the styrene polymerisations [1] also, and the results are shown in Table 11. Comparison of the ratio of the rate at 50% polymerisation calculated from the kinetic order of the initial rate to the initial rate (column 5), with the ratio of the measured rate at 50% polymerisation to the initial rate (column 4) shows that, while they are in approximate agreement for nitromethane solutions, in the absence of solvent the measured values are approximately double that calculated. The " internal " kinetic order for nitromethane solutions is the same as that derived from the initial rates. In the absence of solvent the rate at 50% conversion is nearly half the initial rate, implying that the rate of reaction is dependent on a lower power of [M] and [C] than is the initial rate. If the internal order was $-d[M]/dt = k[M][C]$, then, if x is the amount of monomer polymerised at time t, and b is the ratio of monomer to catalyst molecules combined in the polymer,

$$-d[M]/dt = k([M]_0 - x)([C]_0 - x/b)$$

and log $[([M]_0 - x)/(b[C]_0 - x)]$ should be linear in t. This holds for reactions in absence of solvent (Fig. 4). Since $b[C]_0 \gg x$, the consumption of catalyst has relatively little influence on the internal rate, and log $[[M]_0/([M]_0 - x)]$ is also linear in t (Fig. 4). The internal rate therefore depends on the first power of the monomer concentration but the dependence on catalyst concentration cannot be accurately obtained. It may be that, in non-polar media only, the rate of initiation becomes independent of monomer concentration after the initial stages of the reaction are over.

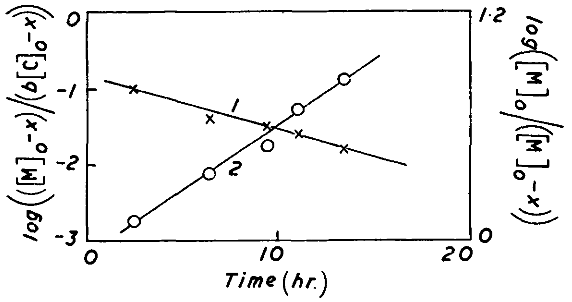


FIG. 4. *Internal order of reaction for trichloroacetic acid catalysis in ethylene dichloride solution* (25°).

1, log $[([M]_0 - x)/(b[C]_0 - x)]$; 2, log $[[M]_0/([M]_0 - x)]$.

EXPERIMENTAL

Materials were purified as already described [1, 5] and rates were measured by the methods used for styrene [1] except that the sealed-tube technique was always used in preference to the viscosity method. Measurements of residual monomer and acid concentrations, polymer molecular weights, viscosities and infrared spectra were made in the same way as for styrene.[1] Catalytic microhydrogenation was performed with palladium-charcoal. The procedure for the extraction of the polymers has also been described.[5]

Low-molecular weight polymer was fractionated along a horizontal temperature gradient under vacuum (Dainton and Tomlinson [6]). The polymer was contained in a flask connected through a segmented horizontal tube 100 cm. long having a series of constrictions along it to a vacuum pump *via* a liquid-air trap which collected unchanged monomer and solvent still contaminating the polymer. The horizontal tube was surrounded by a jacket containing 4 horizontal heating elements of constantan wound so that the heating decreased along the tube. Two thermometers measured the temperature at the ends of the tube. Asbestos plugs prevented the circulation of air in the jacket. The temperature gradient could be varied from 20—50° to 20—200° with an external resistance. During a few hours the polymer separated into fractions along the horizontal tube, the constrictions facilitating the separate removal of the fractions. The pressure in the apparatus was kept at about 0·5 mm. No degradation or loss of chloroacetate end groups occurred during fractionation.

ERRATA

Part X, *J.*, **1957**, 3634, equation (14) *should read* $V_p = -d[M]/dt = k_p k_i K_1[M]^2[C]^2/k_t$.
Part X, *J.*, **1957**, 3639, line 17, *for* $E_1 = E_2 + E_3 - E_1$ *read* $E_i = E_2 + E_3 - E_1$.
Part IX, *J.*, **1957**, 3629, Table 4, heading, *for* below 30·4° *read* " below −30·4°."

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