716. *The Kinetics of Catalytic Polymerisations. Part VII.* Kinetics of the Polymerisation of Styrene catalysed by Di- and Tri-chloroacetic Acid.*

By C. P. Brown and A. R. Mathieson.

The kinetics of the ionic polymerisation of styrene catalysed by di- and tri-chloroacetic acid have been investigated. The dependence of the rates on monomer [M] and catalyst [C] concentrations is given by $-d[M]/dt = k_0[M]^2[C]^{3 \cdot 5}$ for the reaction in absence of solvent, $-d[M]/dt = k_0[M]^2[C]^2$ for ethylene dichloride solutions, and $-d[M]/dt = k_0[M]^2[C]$ for nitromethane solutions. Polymerisation does not occur in the complete absence of water and solvent, and in absence of solvent the rate is proportional to water concentration when this is small. The acid catalysts are consumed during the reactions at abnormally high rates. The overall energies of activation lie between 3 and 14 kcal. mole^{-1}, being greater the more rapid the reaction. Increase of the dielectric constant (D) of the medium increases the reaction rate according to $-d[Me]/dt = Ke^{-\alpha D}$($K$ and α are constants). The molecular weights of the polymer lie between 700 and 2300 at 25°, and increase linearly with monomer and with catalyst concentrations. Increased dielectric constant causes increased molecular weight, such that $\log M \propto (D - 1)/(2D + 1)$ and $\log 1/M$ decreases linearly with $1/T$. *p*-Benzoquinone (Q) retards the polymerisations, the rate becoming proportional to $[Q]^{-\frac{1}{2}}$, and it also reduces the molecular weights of the polymer. The quinone is converted into the red ion QH_2^{2+} and finally into quinhydrone; a mechanism for this inhibition is formulated. Acetone, nitrobenzene, and 1 : 3 : 5-trinitrobenzene inhibit the polymerisation.

Chloroacetic acids are very much weaker polymerisation catalysts than the metal halides. Nevertheless, in the presence of di- or tri-chloroacetic acid, styrene is converted quantitatively into a white polymer at room temperature. The rates of these reactions are linear frequently up to as much as 30% polymerisation. Trichloroacetic acid is a stronger catalyst than dichloroacetic acid, and monochloroacetic acid does not polymerise styrene under normal conditions, though it will polymerise the somewhat more reactive α-methylstyrene. These reactions occur much more rapidly in media of high dielectric constant, such as nitromethane or ethylene dichloride, than in benzene or without solvent. Quinones and nitro-compounds retard, but do not completely inhibit, the polymerisations and their use results in polymers of lower molecular weight. In the complete absence of solvent and water there is no reaction. Lowering the temperature markedly decreases the reaction rates and the polymers are then of greater molecular weight.

The rates are extremely sensitive to the reactant concentrations and this, together with the weakness of the catalysts, makes it necessary to study the reactions at catalyst concentrations higher than would otherwise be desirable. Hence the catalyst solutions cannot be treated as ideal when the kinetics are being interpreted in terms of mechanisms. We now report the influences of reactant concentration, water, retarders, temperature, and dielectric constant on the rate of the polymerisation of styrene catalysed by di- and tri-chloroacetic acid and on the constitution of the polystyrene formed. Some of these results have already been summarised.[1]

Results and Discussion

Quantitative Nature of the Polymerisations.—For a detailed kinetic analysis it must be established that the conversion of monomer into polymer is quantitative and that no

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* Part VI, preceding paper.

[1] Brown and Mathieson, *Ricerca sci.*, 1955, **25**, Sup. Simp. Int. Chim. Macromol.

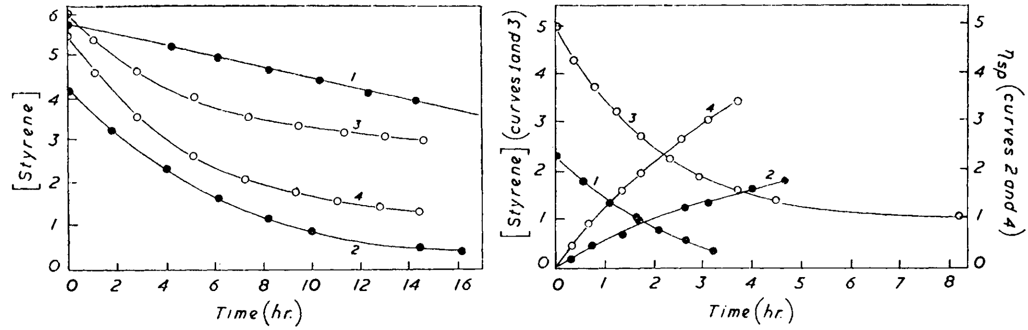
monomer is consumed in side reactions. Solutions of known concentrations of styrene and trichloroacetic acid in ethylene dichloride were allowed to react to given degrees of monomer conversion, and the quantities of polymer formed were measured. The results (Table 1) indicate that the polymerisation is fully quantitative, the agreement between the experimental amounts of polymers obtained and those calculated on the assumption of quantitative polymerisation being within experimental error.

TABLE 1. *Quantitative monomer polymerisation*

Initial monomer concn. (moles $l.^{-1}$)	1·36	1·36	1·97	2·63
Monomer conversion (%)	97·4	97·4	56·7	83·4
Wt. of monomer converted per 100 g. of solution	13·81	13·81	11·63	22·85
Wt. of polymer obtained per 100 g. of solution	13·68	13·95	11·58	23·10

Rates of the Polymerisations in the Pure Monomer.—Typical reaction–time curves are shown in Figs. 1 and 2. The reproducibility of the reaction rates is illustrated in Fig. 3, and is clearly of a high order, particularly in the slower reactions. Table 2 shows the initial reaction rates for different reactant concentrations.

FIGS. 1 and 2. *Typical reaction–time curves for the bulk polymerisation.*



Dichloroacetic acid catalysis, 1, 2; trichloroacetic acid catalysis, 3, 4.

TABLE 2. *Dependence of initial rates (moles $l.^{-1}$ sec.$^{-1}$) of the polymerisation on initial concentrations (no solvent).*

Dichloroacetic acid						
[M]	4·20	4·40	4·60	5·00	5·30	5·80
[C]	4·90	4·50	4·10	3·80	3·60	3·00
10^6 × Rate	13·7	9·50	7·50	6·50	6·18	2·92
Trichloroacetic acid						
[M]	4·90	5·20	5·30	5·60	5·80	6·00
[C]	3·90	3·60	3·20	2·50	2·10	1·70
10^4 × Rate	2·85	2·32	1·52	0·518	0·367	0·157

Since the rates of polymerisation depend on the water concentration when this is below a certain value, the reactions were carried out at a constant concentration of water of 0·70 mole $l.^{-1}$. Above 0·60 mole $l.^{-1}$ of water the rates are of zero order with respect to the water concentration.

The dependence of the initial rate of polymerisation, for both di- and tri-chloroacetic acid catalysis, is given by

$$-d[M]/dt = k_0[M]^2[C]^{3\cdot5} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where [M] and [C] are the *initial* concentrations of monomer and catalyst respectively and k_0 is the overall rate constant. At 25° k_0 is 7·3 × 10^{-8} for dichloroacetic acid and

3·1 × 10^{-6} for trichloroacetic acid, and so the relative rates for the two acids are 1 : 43. The acid dissociation constants are in the ratio 1 : 24.

In the complete absence of water and solvent dichloroacetic acid does not catalyse the polymerisation of styrene, so that water is a cocatalyst for this reaction. Fig. 4 shows the way in which the reaction rate is influenced by the water concentration. At low concentrations of water the rate is directly proportional to it, but at higher concentrations of water the rate becomes independent of it. Still higher concentrations of water (not shown in Fig. 4) reduce the rate. At low water concentrations the initial rate obeys

$$-\mathrm{d}[M]/\mathrm{d}t = k_0'[M]^2[C]^{3\cdot5}[H_2O] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

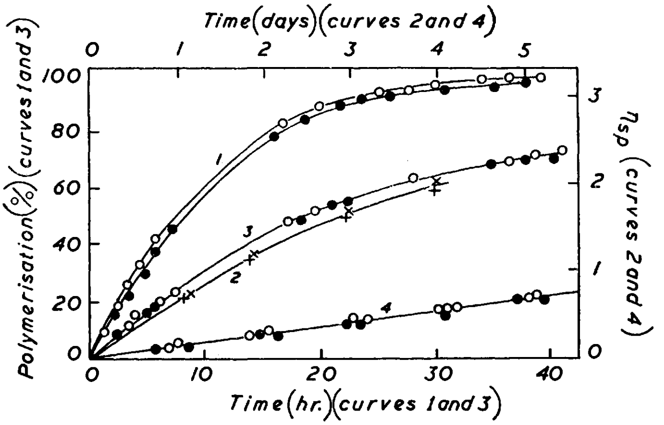


FIG. 3. *Reproducibility of the bulk polymerisation.*

Trichloroacetic acid catalysis, 1, 2; dichloroacetic acid catalysis 3, 4.

FIG. 4. *Dependence of the dichloroacetic acid-catalysed polymerisation upon water concentration.*

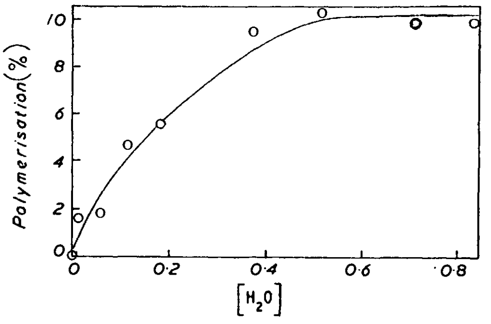
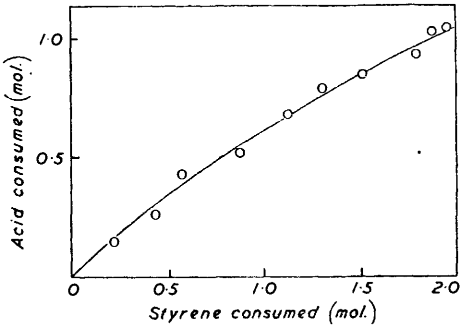


FIG. 5. *Consumption of the dichloroacetic acid catalyst.*



Initial molar concns.; acid 1·7, styrene 6·1.

The acid catalysts are consumed during polymerisation, as can be demonstrated by direct titration during the reaction as well as by incorporation of catalyst in the polymer. Plots of residual monomer and catalyst concentrations during reaction show a rapid consumption of catalyst compared with that of monomer in the initial stages of the reaction. For dichloroacetic acid the mole ratio (acid consumed) : (monomer consumed) is as low as 0·5 for the first 10% of the reaction. The ratio falls as reaction proceeds, reaching 1 : 15 at 90—100% polymerisation. A typical plot of acid consumed against monomer consumed is shown in Fig. 5 for the initial stages of a reaction, and Table 3 shows values for both di- and tri-chloroacetic acid catalysis. For trichloroacetic acid the ratio never falls much below 0·5, and this suggests extensive formation of monomer–catalyst or polymer–catalyst complex.

Rates of the Polymerisations in Ethylene Dichloride.—It was not possible to influence the rate of polymerisation by decreasing the water concentration to very low values for

TABLE 3. *Relative rates of consumption of monomer and catalyst (catalyst consumed per mol. of monomer consumed).*

Monomer conversion (%)	10	20	30	50	100
Dichloroacetic acid (mol.)	0·498	0·283	0·200	0·121	0·0641
Trichloroacetic acid (mol.)	1·19	0·953	0·885	0·552	0·449

TABLE 4. *Dependence of initial rates (moles l.$^{-1}$ sec.$^{-1}$) of the polymerisation in ethylene dichloride on initial concentrations at 25°.*

Dichloroacetic acid					
[M]	2·00	2·08	2·18	3·50	4·72
[C]	2·20	4·28	3·32	3·00	2·56
10^6 × Rate	0·917	4·17	2·78	5·78	7·62

Trichloroacetic acid					
[M]	1·44	1·48	1·70	1·78	1·89
[C]	1·80	0·84	1·60	1·00	1·30
10^5 × Rate	2·52	0·550	2·22	1·03	3·18

ethylene dichloride solutions. It may be that the increased dielectric capacity of the medium favours the autoprotolysis of the catalyst, or that the solvent can act as a co-catalyst. At fairly large water concentrations the rate decreased steadily on increase of water concentration. The dependence of the rate of polymerisation on the reactant concentrations is shown in Table 4. For both acids the kinetics of the reactions are accurately described by

$$-d[M]/dt = k_0[M]^2[C]^2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The values of k_0 are $3{\cdot}12 \times 10^{-5}$ for dichloroacetic and $1{\cdot}85 \times 10^{-3}$ for trichloroacetic acid, the rates being in the ratio 1 : 59. The change in the dependence of the rate upon catalyst concentration on introduction of ethylene dichloride into the systems is most striking.

The catalysts are again consumed during reaction, and Table 5 shows the relative rate of consumption of monomer and catalyst for both acids. In both cases the mole ratio (acid consumed) : (monomer consumed) increases steadily throughout the reaction, for trichloroacetic acid the ratio being again much higher and subject to a much smaller increase.

TABLE 5. *Relative rates of consumption of monomer and catalyst in ethylene dichloride (catalyst consumed per mol. of monomer consumed).*

Monomer conversion (%)	10	20	30	50	100
Dichloroacetic acid (mol.)	0·316	0·213	0·160	0·133	0·0978
Trichloroacetic acid (mol.)	0·424	0·411	0·408	0·389	0·318

Rates of the Polymerisations in Nitromethane.—The reactions are more rapid in nitromethane, and Table 6 shows the results for di- and tri-chloroacetic acid catalysis. Eqn. (4) accurately described the kinetics :

$$-d[M]/dt = k_0[M]^2[C] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The values of the overall rate constant are $k_0 = 1{\cdot}6 \times 10^{-4}$ for dichloroacetic and $7{\cdot}3 \times 10^{-3}$ for trichloroacetic acid, the relative rates being 1 : 46. The consumption of the acid catalyst cannot be investigated in nitromethane by the method used for polymerisations without solvent and in ethylene dichloride.

TABLE 6. *Dependence of initial rates (moles l.$^{-1}$ sec.$^{-1}$) of the polymerisation in nitromethane on initial concentrations at 25°.*

Dichloroacetic acid					
[M]	1·03	1·17	1·32	1·42	1·59
[C]	2·01	2·10	1·98	2·11	1·98
10^6 × Rate	3·33	6·82	9·17	12·2	14·3

Trichloroacetic acid					
[M]	1·70	1·93	2·00	2·95	3·13
[C]	1·01	1·60	1·21	1·29	1·02
10^4 × Rate...	1·00	3·00	2·00	5·50	4·33

The reaction rate decreases with increased concentration of water, and in this solvent the conductance of the reactant solution has been measured for different water concentrations at constant monomer and acid concentration. The results (Table 7) show that increase in water concentration increases the conductance but decreases the rate of

TABLE 7. *Conductance of reactant solutions at 25°.*

(Monomer concn. = 1·61, catalyst concn. = 2·11 moles $l.^{-1}$.)

Water concn. (moles $l.^{-1}$)	~0	0·15	0·36	0·78	1·01	2·37
Equivalent conductance (ohm^{-1} $cm.^{-1}$)	~0	0·0793	0·168	0·301	0·497	1·26
10^3 Reaction rate (moles $l.^{-1}$ $sec.^{-1}$)	1·45	1·42	1·33	1·18	1·50	0·60

polymerisation. The presence of a measurable concentration of hydrogen ion does not appear to increase the reaction rate. It may be that competition occurs between the water and the monomer for the proton of the acid, or alternatively that the ionisation step is not rate-determining.

Temperature-dependence of the Reaction Rates.—Polymerisations catalysed by both di- and tri-chloroacetic acid were performed without and with solvents at 0°, 25°, and 40°. Agreement with the Arrhenius equation was found in all cases. Values of the overall energy of activation (E_0) for the reactions were calculated from the results and these are shown in Table 8.

TABLE 8. *Overall energy of activation* (*kcal. mole*$^{-1}$).

Solvent	Styrene	C_2H_5Br	$C_2H_4Cl_2$	$C_2H_5{\cdot}NO_2$	$CH_3{\cdot}NO_2$
Dielectric constant	2·0	4·87	10·5	19·7	39
E_0, Dichloroacetic acid	5·5	3·0	6·0	—	8·0
E_0, Trichloroacetic acid	9·0	3·0	8·0	10·0	14·0

It is significant that, if polymerisations without solvent are not counted, the energy of activation increases with increasing dielectric constant of the solvent. Increased dielectric constant also increases the rate of the reaction and the apparent anomaly exists that the reactions proceed the more rapidly the greater the energy of activation. This has been noticed for ionic polymerisations before,[2] values of E_0 of 10·0 and 15·0 kcal. mole^{-1} being obtained for the polymerisation of octyl vinyl ether catalysed by iodine in hexane and ethylene respectively. Also, for the polymerisation of styrene catalysed by stannic chloride,[3] it was found that $E_0 = 3{\cdot}0$ kcal. mole^{-1} for carbon tetrachloride solutions, and $E_0 = 4{\cdot}5$ kcal. mole^{-1} for ethyl chloride solutions.[4] An interpretation of this effect in terms of complex-formation between monomer and catalyst will be given in Part X.

Variation of the Reaction Rates with the Dielectric Constant of the Medium.—The relatively large concentrations of monomer and catalyst employed make it essential to measure the dielectric constant of the reaction solutions, since it cannot be assumed to be equal to that of the solvent. The rates of the polymerisation of styrene catalysed by trichloroacetic acid in a series of benzene–nitromethane mixtures and in a series of benzene–ethylene dichloride mixtures were measured viscosimetrically, and can be compared for experiments at the same monomer and catalyst concentrations by comparing the values of the specific viscosity (η_{sp}) of the solutions after the same short time interval, during the initial period of the reaction when η_{sp} is a linear function of time. Fig. 6 shows these results, from which

$$-d[M]/dt = Ke^{-\alpha D} \qquad \text{. . . . . . . (5)}$$

where K and α are constants for all mixtures of the same two solvents.

Various equations connecting the rate of chemical reaction with the dielectric constant of the medium have been suggested.[7]

$$\ln k = B + C(D - 1)/(2D + 1) \qquad \text{. . . . . . . (6)}$$

$$\ln k = B + C(1/D - 1) \qquad \text{. . . . . . . (7)}$$

Neither of these expressions agrees with our results [eqn. (5)].

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[2] Eley and Richards, *Trans. Faraday Soc.*, 1949, **45**, 425, 436.

[3] Williams, *J.*, 1938, 246, 1046.

[4] Gantmaker and Medvedev, *Zhur. fiz. Khim.*, 1949, **23**, 516.

[5] Glasstone, Laidler, and Eyring, "Theory of Rate Processes," McGraw-Hill, New York, 1945, p. 419.

[6] Laidler and Eyring, *Ann. New York Acad. Sci.*, 1940, **39**, 303.

[7] Wassermann *et al.*, *Nature*, 1951, **168**, 459; *J. Polymer Sci.*, 1952, **8**, 157.

The increase in reaction rate with dielectric constant demonstrates the ionic nature of these polymerisations, and the magnitudes of the energies of activation and polymer molecular weights are also those to be expected for ionic polymerisations.

Molecular Weights of the Polymers.—The number-average molecular weights of the polymers, measured cryoscopically, were 700—2300, and depended on the reaction conditions, but showed slight variation between the two catalysts. In ethylene dichloride and in nitromethane, the molecular weight of the polymer varied with the extent of reaction and with the initial monomer concentration (Table 9) at constant trichloroacetic acid concentration. These results show that the molecular weight increases linearly with the monomer concentration. In ethylene dichloride the recorded molecular weight takes account of all the polymer formed up to the given degree of monomer conversion. For monomer concentrations between 1·0 and 5·0M the molecular weight (M) is given by

$$M = 1100 + 200[\mathrm{M}] \qquad (8)$$

and

$$M = 975 + 70[\mathrm{M}] \qquad (9)$$

for nitromethane and ethylene dichloride solutions respectively.

TABLE 9. *Dependence of molecular weight on monomer concentration at* 25°.

	Nitromethane				Ethylene dichloride				
[M] (initial)	1·21	2·42	3·63	4·84	4·15	4·15	4·15	4·15	4·15
Conversion (%)	20·15	21·10	20·36	20·11	19·8	37·2	51·2	63·1	79·9
M	1300	1650	1850	2000	1250	1210	1190	1190	1150

TABLE 10. *Dependence of molecular weight on catalyst concentration at* 25°.

	Nitromethane				Ethylene dichloride			
[C]	1·20	2·40	3·60	4·80	0·70	1·80	3·30	5·00
M	1300	1600	1800	1950	1150	1300	1500	1700

The molecular weight also increases linearly with the catalyst concentration, and Table 10 shows this effect for trichloroacetic acid catalysis.

The dependence of molecular weight on catalyst concentration can be given as

$$M = 1000 + 190[\mathrm{C}] \qquad (10)$$

and

$$M = 1100 + 120[\mathrm{C}] \qquad (11)$$

for nitromethane and ethylene dichloride respectively. Dependence of the molecular weight on catalyst concentration is unusual for ionic polymerisation, but has been observed for other systems catalysed by trichloroacetic acid.[7]

The influence of the dielectric constant of the medium on the molecular weight was studied by carrying out the reaction at constant concentrations of monomer and catalyst in different solvents. Table 11 shows that increased dielectric constant increases the molecular weight. The results obey an equation analogous to eqn. (6) with molecular weight substituted for reaction rate, *i.e.*,

TABLE 11. *Dependence of molecular weight on dielectric constant at* 25°.

Solvent	*cyclo*Hexane	$C_2H_4Cl_2$	$C_2H_5{\cdot}NO_2$	$CH_3{\cdot}NO_2$
D	1·9	8·7	20	31
M (trichloroacetic acid)	800	970	1090	1160
M (dichoroacetic acid)	720	910	980	1050

$$\log M = B + C(D - 1)/(2D + 1) \qquad (12)$$

in which $C = 0{\cdot}23$ for both acids, and $B = 2{\cdot}85$ and $2{\cdot}90$ respectively for di- and tri-chloroacetic acid.

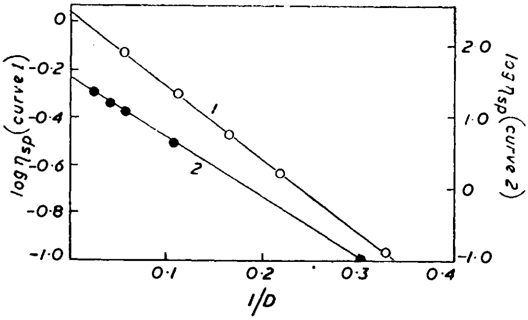
The variation of molecular weight with the temperature of reaction was studied over the range −80° to +40° with trichloroacetic acid and ethyl bromide as solvent. The rate at —80° was so small that the solution had to be allowed to react for 6—8 weeks in a sealed tube in the dark for sufficient polymer to be formed. Values of $-\log 1/M$ for various values of $10^3/T$ (in parentheses) of 3·03(3·2), 3·10(3·7), and 3·37(5·4) show that log $(1/M)$ decreases linearly with $1/T$. Since the chain length of the polymer (n) is given by the ratio of the rate of propagation to the rate of chain termination, *i.e.*, $n = V_p/V_t$, no chain-transfer being assumed, it follows for spontaneous termination that

$$\ln 1/n = \ln (k_t/k_p[M])(E_p - E_t)/\boldsymbol{R}T \quad . \; . \; . \; . \; . \quad (13)$$

where k_p, k_t, E_p, and E_t are the specific rates and activation energies of propagation and termination. The value of $E_p - E_t$ can be calculated from the results given above to be —850 cal. mole^{-1}.

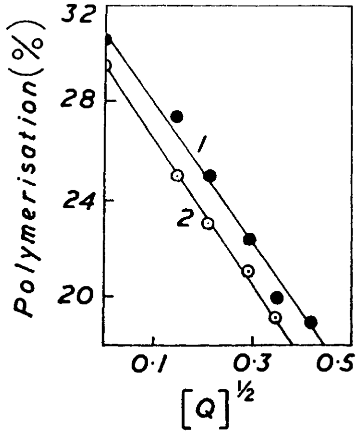
Effect of p-*Benzoquinone on the Polymerisations.*—Quinones retard the chloroacetic acid-catalysed polymerisations in spite of their ionic character, and 1M-quinone can inhibit reaction completely. Lower concentrations retard rather than inhibit, and no induction periods can be observed. Dilute solutions of p-benzoquinone (Q) in either styrene or dichloroacetic acid are the normal yellow colour, but immediately on addition of the second reactant (either dichloroacetic acid or styrene) the solour changes to bright red which after several hours tends to become dark green. In concentrated solutions of quinone the appearance of the red colour is followed by an immediate darkening and the deposition of a dark green precipitate. The precipitate was shown by its m. p., molecular weight, and microchemical and X-ray powder analysis to be quinhydrone. The red colour was shown to be due to the QH_2^{2+} ion, first identified by Mackenzie and Winter,[8] by absorption spectroscopy.

FIG. 6. *Effect of dielectric constant on reaction rate.*



I, Benzene–ethylene dichloride mixtures; II, benzene–nitromethane mixtures.

FIG. 7. *Effect of benzoquinone on the rate of polymerisation of styrene by trichloroacetic acid.*



I, Ethyl bromide solution, after 41 hr.; II, Bulk polymerisation, after 47 hr.

The kinetics of the polymerisation were examined in the presence of different concentrations of benzoquinone, and Fig. 7 shows clearly that the rate of polymerisation is inversely proportional to the square root of its concentration, at constant concentrations of monomer and catalyst, *i.e.*, $-d[M]/dt = k[Q]^{-\frac{1}{2}}$. The molecular weight of the polymer formed at 20% monomer conversion in the presence of benzoquinone (moles l.$^{-1}$, in parentheses) is decreased in proportion to the amount of quinone present, as follows: 1200(0·00), 1100(0·01), 1060(0·05), 1000(0·10), 820(0·50), 530(1·10). All these results can be explained

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[8] Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159.

by supposing that a benzoquinone molecule collides separately with two growing polymer ions (M_n^+):

$$M_n^+ + Q \longrightarrow M_n + QH^+$$

$$M_n^+ + QH^+ \longrightarrow M_n + QH_2^{2+}$$

this leads to the inverse-square-root dependence of the rate on quinone concentration, explains the chain-breaking action of the quinone in reducing the molecular weight, and allows for the formation of the observed ion QH_2^{2+}. To account for the formation of quinhydrone it is necessary to postulate the reaction

$$QH_2^{2+} + Q \longrightarrow Q_2H_2$$

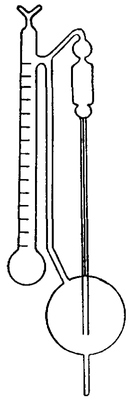
This mechanism of quinone inhibition is similar to that postulated for the inhibition by amines of the stannic chloride-catalysed polymerisation.[9] In that case the amine is supposed to form a stable ion M_n–NR_3^+. This retardation of an ionic polymerisation by quinone implies that quinone inhibition can no longer be taken as a criterion of a free-radical polymerisation.

Other Inhibitors and Retarders.—The polymerisation is completely inhibited by acetone, nitrobenzene, and 1 : 3 : 5-trinitrobenzene, and the formation of stable inhibitor–catalyst complexes is presumably responsible.

EXPERIMENTAL

Materials.—These were purified as in the preceding paper, and kept in sealed tubes or distilled, in dry nitrogen, into the reaction system. Ethyl bromide was treated with concentrated sulphuric acid to remove alcohol, washed with sodium carbonate solution and with water, and distilled from calcium chloride, the middle fraction being collected. Carbon tetrachloride was washed with alcoholic potassium hydroxide, then with water, and distilled from calcium chloride. "AnalaR" benzene was not further purified.

FIG. 8. *Vacuum viscometer.*



The Reaction System.—A high-vacuum glass apparatus was employed. Monomer, catalyst, and solvent were collected in separate sealed tubes, frozen, and the tubes joined to the vacuum system. The whole apparatus was thoroughly evacuated, and the monomer, catalyst, and solvent were separately distilled into a graduated chilled reaction vessel. The frozen reaction mixture was brought rapidly to the reaction temperature and the reaction mixture was run into a series of tubes, or into the vacuum viscometer, which were then sealed off and placed in a thermostat. The reaction was followed either by opening the sealed tubes at different times and titrating the mixture, or by measurement of viscosity. Fig. 8 shows a viscometer, specially designed for measurements under vacuum conditions. Viscometers of 10 and 20 ml. capacity were used.

To vary the water content of the reaction solution an evacuated bulb of approx. 1 l. capacity was allowed to attain the equilibrium water vapour pressure by connecting it to a smaller bulb containing water or ice at a known temperature. The large bulb was isolated and the vapour it contained was then condensed on the chilled reaction mixture.

Since the viscosity of a polymerising solution is a function of the polymer molecular weight as well as of the degree of monomer conversion, the viscosity was calibrated against the reaction rate determined by the sealed-tube method for each range of polymer molecular weight obtained.

The reaction solutions were analysed as in the preceding paper.

Dielectric Constant and Conductance Measurement.—A Marconi Universal bridge (1000 kc./sec.) with a range of 0·1 μμF to 1 F was used, in conjunction with a dielectric-constant cell consisting of three concentric brass tubes (9 cm. long, 2 cm. outside diameter) separated by mica strips, the inner and outer cylinders being joined by a brass strip. The conductance cell was of the standard form and had a cell constant of 0·4515.

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[9] George, Mark, and Wechsler, *J. Amer. Chem. Soc.*, 1950, **72**, 3891; *J. Polymer Sci.*, 1951, **6**, 725.

Molecular Weights of Polymers.—The polymers, extracted and purified as described in the preceding paper, were dissolved in benzene and the molecular weight measured cryoscopically at a series of polymer concentrations, the results being extrapolated to zero concentration.

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