593. *Cationic Polymerisation of a Bicyclopentyl Derivative: Mechanism of Formation of Deeply Coloured, Electrically Conducting Polymers*

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3-(Cyclopenta-2,4-dienyl)cyclopentyl trichloroacetate (I) has been polymerised in benzene under catalysis by acetic, halogenoacetic, hydrochloric, and diphenylphosphoric acids. The catalysis by trichloroacetic acid has also been studied in the presence of acetone, dioxan, water, ethanol, and piperidine, which act as retarders. The products contain end-groups the nature of which depends on the catalyst, and double bonds, some of which are conjugated. This accounts for the bluish-black colour in presence of acids, proton acceptor properties, and electrical conductance.

In the absence of retarders, the rate of polymerisation is first-order with respect to ester (I) and catalyst, the molecular weights being independent of initial concentrations or degree of conversion of ester (I). The initiation is taken to be a relatively slow proton transfer from catalyst to monomer, and the termination a reaction in which the monomer is incorporated into the growing carbonium-ion pair. Structural reasons why interaction of growing species can lead to continuation of growth in the propagation steps, but to cessation of growth in the termination steps, are indicated. The assumption that the initiation is a relatively slow proton transfer is confirmed by a Brönsted type relation between the rate coefficients of initiation and the equilibrium constants of proton transfer, *K*, of the catalysing acids, with a previously described proton acceptor.

Further evidence for the role of proton transfer reactions is the retardation of polymerisation by proton acceptors. This is due to a decrease of the effective catalyst concentration, and to an additional termination step.

CYCLOPENTADIENE and trichloroacetic acid react under specified conditions to form a reactive ester (I), which could be isolated [1] and which is the " monomer " in a subsequent

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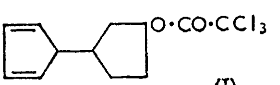
[1] C. F. Blakeley, R. J. Gillespie, L. Roubinek, A. Wassermann, and R. F. M. White, *J.*, **1961**, **1939**.

reaction[2] leading to deeply coloured polymers.[3] If the formation of ester (I) had been overlooked, the observations relating to the overall process cyclopentadiene ⟶ product require different initial and "internal" rates, as in some previously studied cationic polymerisations.[4] The reaction, ester (I) ⟶ product, on the other hand, is kinetically simple.[2] The mechanism which accounts for the observed rate law and molecular weights is rather unusual and we decided, therefore, to study the polymerisation of ester (I) under catalysis by acids of graded strength, and the influence of proton acceptors. The results of this work confirm the earlier postulates and are of general interest for cationic polymerisations.



(I)

These experiments are grouped as follows: (*a*) preparation and characterisation of polymers; (*b*) proton acceptor properties and electrochemical behaviour of polymers; and (*c*) kinetics of polymerisation. Some results of (*a*) and (*b*) are of relevance for a correct interpretation of the kinetics.

EXPERIMENTAL

Starting Materials.—3-(Cyclopenta-2,4-dienyl)cyclopentyl trichloroacetate (I), prepared[1] in batches of about 30 g. was distributed in ten glass containers. After the addition to each sample of about 0·5 g. of solid potassium hydrogen carbonate, the ester was degassed by evacuation to 10^{-3} mm.; the containers were sealed off *in vacuo* and stored at −80°. After a container was opened, the ester was immediately dissolved in benzene, the solution, with some solid potassium hydrogen carbonate, being introduced into a storage vessel, V, fitted with a filter plate and two vacuum taps. The vessel was then degassed and the whole stored at 0°. Aliquots of the filtered ester solution could be transferred to an evacuated second vessel, V_1, without oxygen being admitted to vessel V (see Figure 1). Concentration determinations of the ester solution were carried out by alkaline hydrolysis in benzene–ethanol. Stock solutions older than about 10 days were discarded.

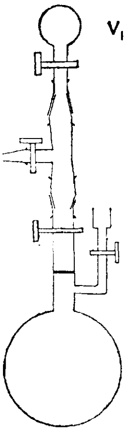


FIGURE 1. Reaction vessels V and V_1 (see text)

AnalaR benzene was refluxed with potassium, fractionated, and stored over sodium. AnalaR tri- and mono-chloracetic acids and diphenylphosphoric acid, recrystallised from cyclohexane, were dried over phosphorus pentoxide. Trifluoroacetic acid was kept over anhydrous sodium sulphate and fractionated *in vacuo*. Dichloroacetic acid and acetic acid were purified by fractional crystallisation. Purified benzene was introduced into a vessel, V_2, fitted with vacuum taps, adaptors, and gas inlet, protected from atmospheric moisture; hydrochloric acid, generated from sodium chloride and sulphuric acid and dried over phosphorus pentoxide, was slowly bubbled through the benzene in a vessel, V_2, thereby removing dissolved oxygen. The resulting hydrochloric acid solution, 0·3—0·4N, was stored in the dark. Aliquots of the solution,

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[2] J. Murphy, L. Roubinek, and A. Wassermann, *J.*, 1961, 1964.

[3] P. V. French, L. Roubinek, and A. Wassermann, *J.*, 1961, 1953.

[4] See, *e.g.*, "The Chemistry of Cationic Polymerisation," ed. P. H. Plesch, Pergamon, London, 1963.

removed by overpressure of nitrogen, could be introduced into evacuated containers, light-absorption or conductance cells, or specially constructed titration vessels, without admission of atmospheric oxygen or moisture and without loss of volatile acid. Optically clear solutions of hydrochloric acid in benzene require careful purification and drying of the solvent. Piperidine, dried over barium oxide, and water, were redistilled. Acetone, dioxan, and ethanol AnalaR, and the antioxidant α-tocopherol, were used, in most experiments without purification; control tests established that refractionation of the benzene mentioned above and of the retarders had no significant influence on the kinetics of polymerisation.

Polymers.—These were prepared from solutions of ester (I), 10^{-5}—10^{-4}M with respect to α-tocopherol, which were either degassed and kept in evacuated sealed-off containers, or kept in an atmosphere of pure nitrogen. In the polymerisation of ester (I), trichloroacetic acid is released. The influence of this reaction must be swamped by adjustment of the concentration of the added catalyst and degree of conversion. Before the polymers were isolated, the acids (with the exception of acetic acid) were removed by treatment with solid potassium hydrogen carbonate, or by shaking the benzene solution with aqueous sodium hydroxide. The benzene was distilled off below 30°, until the solution was about 5% with respect to polymer; this was precipitated with ethanol or pentane (10 volumes), centrifuged off, and dried *in vacuo*. The product, purified by reprecipitation from benzene, was distributed in small glass tubes, which were evacuated and sealed off. Shortly before each experiment one of the tubes was opened, and material not used was discarded, thereby avoiding unequal air oxidation of the bulk polymer. Care was taken to expose the polymers to air for as short a time as possible. Oxidative attack was further reduced by making the reaction mixture about 10^{-4}M with respect to α-tocopherol. Without these precautions the capacity of the polymers to bind protons is reduced.

The molecular weights of the polymers were measured in benzene at 25·0°, with a Mechrolab vapour-phase osmometer, model 301A. At least four concentrations, c, were tested; c_1 was at least $8c_4$ and the required extrapolation to $c = 0$ could be made without difficulty. Control experiments showed that the loss of low-molecular-weight fractions during reprecipitation is not significant. Three to five batches of each polymer were analysed for carbon, hydrogen, and halogen or phosphorus, the figures in lines 2—6 of Table 2 being mean values. Alkali consumption in benzene–ethanol was determined by electrometric titration;[3] bromine uptake was measured as previously described.[1] Control experiments were carried out to show that no trans-esterification occurs. Polymer A, for instance, which contains a trichloroacetate grouping, was dissolved in benzene, 0·9M in monochloroacetic acid; after 13 days at 20°, under nitrogen, the polymer was unchanged.

Optical densities were measured with a Unicam S.P. 500 instrument, using cells of optical path length 0·1—4 cm. and a wavelength coinciding with the position of one of the peaks in the electronic spectrum of the product. Proton transfer equilibria were measured in the presence of air with solutions stabilised by 10^{-4}M-α-tocopherol. The optical densities, d, of the polymer–acid adducts were nevertheless time-dependent and results were calculated from d-values extrapolated to the time of mixing polymer and acid. In the kinetic tests, on the other hand, cells of the type shown in Figure 1, ref. 3, were used; at zero time the degassed reaction mixture was introduced without coming into contact with air. The d-values did not drift if the oxygen partial pressure was below 1 mm. In the experiments with the volatile hydrochloric acid, solutions were filled to a level just below the taps of light absorption or conductance cells (see below) to avoid evaporation of the acid from the solution.

Electrical resistances were measured at 25·0° ± 0·01° by a d.c. technique, using a Vibron electrometer, model 33 B, a current and resistance unit model A 33 B, and conductance cell shown in Figure 2, through which a stream of dry nitrogen presaturated with benzene was passed. The specific electrical conductance, κ, did not drift after establishment of the temperature equilibrium. The electrical conductance of solutions of the volatile hydrochloric acid was measured in the cell shown in Figure 3, in which the mixture could be magnetically stirred. The polarity of the electrodes of both cells (applied potential 2 volts) was frequently reversed. Cell constants were measured with a potassium chloride solution and an a.c. bridge.

Kinetics.—The specific electrical conductance of benzene solutions containing ester (I) together with an acid catalyst increases with increasing time, while the initially colourless reaction mixture becomes gradually bluish-black. These effects are due to the formation of polymers containing conjugated double bonds which give rise to relatively large electrical conductance and optical densities (see ref. 3). Thus, the kinetics of polymerisation of ester (I) can be studied by measuring the increase of polymer concentration either spectrophotometrically, as previously [2] described, or conductimetrically.

The catalysis by hydrochloric acid was studied spectrophotometrically. Hydrochloric acid concentrations were determined at the end of each run by transferring the mixture from the evacuated light-absorption cell, through suitable adaptors, into weighed evacuated titration vessels. The concentrations agreed to within ±1% with values deduced from the titre of the stock solution. The analysis of polymer A_3 shows that the hydrochloric acid does not add to the double bonds in the repeating C_{10}-units.

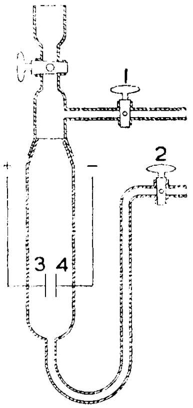

FIGURE 2. Cell for measuring the electrical resistance of benzene solutions in a stream of nitrogen. The inlets of the taps 1 and 2 were connected with U-tubes containing silica gel. The electrodes 3 and 4, and also the electrodes of the cell shown in Figure 3, were blank platinum sheets

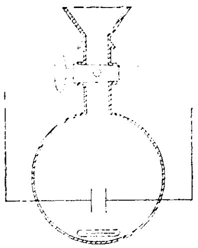

FIGURE 3. Cell for measuring the electrical resistance of benzene solutions of hydrochloric acid

The rate of polymerisation under catalysis by the other acids was measured conductimetrically. Conversion of electrical resistance of the solution, as measured at time *t*, into polymer concentration at time *t*, required calibration. For this, solutions were prepared of the same catalyst concentration, but of different polymer concentration, the resistance of each of these solutions being determined. The results enabled one to construct, for each catalyst concentration, a calibration curve of the type shown (Figure 4). Control experiments showed that the specific electrical conductance of a solution containing polymer and acid is not significantly altered on addition of ester (I) and that careful drying (see ref. 2) has no marked influence on the conductance of these solutions or on the rate of polymerisation. Experiments were carried out to show that velocity constants relating to a given catalyst, and determined either spectrophotometrically or conductimetrically, agreed within the limits of the experimental errors given in Table 8. Details of the conductimetric technique are given in the following paragraphs.

Chloroacetic and diphenylphosphoric acids. Ester (I) and acid were mixed in the conductance cell (Figure 2) through which a stream of nitrogen passed throughout the run. Frequent resistance measurements were made without removing the cell from the thermostat-controlled bath.

Trifluoroacetic acid. The same technique was used, except that the bubbling of nitrogen was stopped after the reactant and the catalyst had been mixed.

Trichloroacetic acid and retarders. The acid and the retarder were mixed in the conductance cell; when air was replaced by nitrogen and temperature equilibrium was reached, ester (I) was added and further resistance measurements were made in a stream of nitrogen. Control experiments were carried out in which ester and retarder were mixed and acid was added afterwards. There was no detectable difference of the rate of polymerisation.

Acetic acid. The catalytic rate was so slow that the reaction mixture could not be kept throughout the run in the conductance cell. Solutions of ester (I) and acid were distributed in sets of glass vessels, which were evacuated, sealed off, and placed in a thermostat-controlled bath. At times t_1, t_2, . . . a container was opened and, after the solution had been transferred to the conductance cell, the resistance Ω_1, Ω_2, ... was measured under nitrogen.

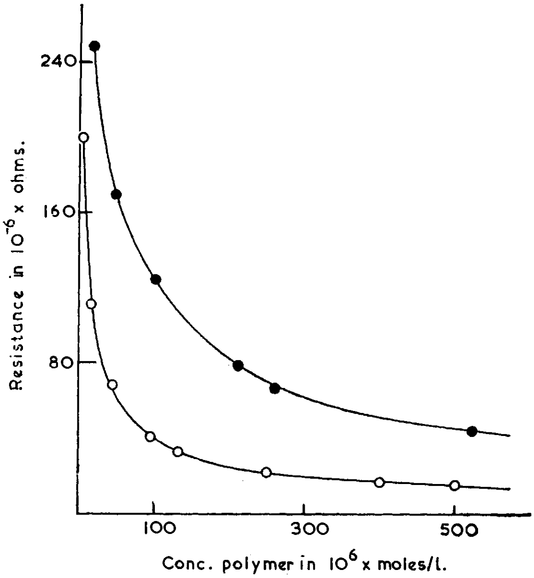

FIGURE 4. Typical calibration curves; solvent benzene, 25·0°

○, 0·448M-trifluoroacetic acid; polymer A_4, cell constant 0·166 cm.$^{-1}$

●, 0·312M-trichloroacetic acid, 0·412M-acetone; polymer A_{10}, cell constant 0·153 cm.$^{-1}$

Calculation of equilibrium and velocity constants. The polymers, P, are reversible proton acceptors and react with acids, HB, as follows [3]

$$\mathrm{P} + \mathrm{HB} \overset{K}{\rightleftharpoons} \mathrm{PH}^+ \cdots \mathrm{B}^- \qquad (1)$$

where $\mathrm{PH}^+ \cdots \mathrm{B}^-$ is a deeply coloured electrically conducting ion pair, formed by proton transfer from HB to P, and K is the equilibrium constant of proton transfer. The electrical conductance of solutions containing the species $\mathrm{PH}^+ \cdots \mathrm{B}^-$ is due to dissociation into free ions.

$$\mathrm{PH}^+ \cdots \mathrm{B}^- \overset{K_d}{\rightleftharpoons} \mathrm{PH}^+ + \mathrm{B}^- \qquad (2)$$

The protonated polymer cation, PH^+, and the counterion, B^-, are the carriers of the current and K_d is the ion-pair dissociation constant. The experimental determination of K and K_d has been carried out by previously described [3] spectrophotometric and conductimetric techniques. The former is essentially the same as that used for measuring indicator constants in an aprotic solvent; [5] it is based on the determination of the ratio

$$\beta = [\mathrm{PH}^+ \cdots \mathrm{B}^-]/[\mathrm{P}] = (d - d_0)/(d_\infty - d) \qquad (3)$$

where d, d_0, and d_∞ are optical densities of solutions containing, respectively, P and $\mathrm{PH}^+ \cdots \mathrm{B}^-$, P without $\mathrm{PH}^+ \cdots \mathrm{B}^-$, and $\mathrm{PH}^+ \cdots \mathrm{B}^-$ without P. According to equation (1), log K is the intercept of linear plots of log β versus log [HB]. The optical density, d_∞, could be directly measured if the proton donors were trichloro-, dichloro-, and trifluoro-acetic and hydrochloric acids. In the reactions with acetic, monochloroacetic and diphenylphosphoric acids, on the other hand, d_∞ had to be calculated; for this, it was assumed that the extinction coefficients, ε, of these acid adducts are identical with the known ε values of ion-pairs containing trichloroacetic acid and polymer A (cf. ref. 3).

In calculating ion-pair dissociations constants, K_d, molar electrical conductances, Λ, of the

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[5] See, *e.g.*, R. P. Bell and J. W. Bayles, *J.*, 1952, 1518.

ion-pairs were measured as described before [3] and an empirical extrapolation method [3] was used to estimate Λ_0, the molar electrical conductance at infinite dilution. Equation (2) requires that

$$-\log \Lambda = \tfrac{1}{2} \log [\mathrm{PH}^+ \cdots \mathrm{B}^-] - \tfrac{1}{2} \log K_\mathrm{d} - \log \Lambda_0 \tag{4}$$

If $\log \Lambda$ is plotted against $\log [\mathrm{PH}^+ \cdots \mathrm{B}^-]$, straight lines of slope 1/2 should be obtained, the intercepts enabling K_d to be calculated. Numerical values of the constants K and K_d are relevant, for reasons indicated below. These parameters, however, are not thermodynamic equilibrium constants, because activity corrections have been neglected.

In studying the kinetics of the polymerisation, the concentration of the acids was large compared with that of the monomer, so that the rate could be characterised by first-order velocity constants, k'. If the degree of conversion of ester (I) was sufficiently large, evaluation was carried out with the help of Guggenheim's method.[6] In experiments with weak acids or with retarders, k' was obtained from linear concentration–time plots of the type shown in (Figure 6b), and the expression

$$k' = nv_0/[(\mathrm{I})]_0 \tag{5}$$

where n is the number average degree of polymerisation, v_0 is the initial rate of polymer formation, $\{\mathrm{d}[\text{polymer}]/\mathrm{d}t\}_{t\to 0}$, and $[(\mathrm{I})]_0$ is the initial concentration of the monomer. Catalytic second-order rate constants were calculated from

$$k = k'/[\mathrm{HB}] \tag{6}$$

$$k_p = k_p'/[\mathrm{HB}] \tag{7}$$

the subscript indicating that the rate constants relate to experiments with retarders and [HB] being the stoicheiometric acid concentration. A different velocity constant, k_p^F, is defined by

$$k_p^\mathrm{F} = k_p'/[\mathrm{HB}]_\mathrm{F} \tag{8}$$

In order to estimate $[\mathrm{HB}]_\mathrm{F}$, the concentration of " free " acid which is not " combined " with the retarder, an indicator method has been used. In the presence of a colourless proton-acceptor (retarder) the ratio $[\mathrm{PH}^+ \cdots \mathrm{B}^-]/[\mathrm{P}]$ is given by

$$\beta_p = (d_p - d_0)/(d_\infty - d_p) \tag{9}$$

where d_p is the optical density of a solution containing P, $\mathrm{PH}^+ \cdots \mathrm{B}^-$, and the retarder, and the other symbols have the same significance as in equation (3). The concentration of the free acid, $[\mathrm{HB}]_\mathrm{F}$, is given by

$$[\mathrm{HB}]_\mathrm{F} = \beta_p/K \tag{10}$$

For approximate numerical calculations it is assumed, as in previous work,[7] that the equilibrium coefficient, K, is not altered on addition of retarder.

In principle, all the polymers here considered are suitable proton acceptors for indicator studies because equilibrium (1) is stoicheiometrically simple. For the experiments to be described, polymer A (see ref. 3) was selected because it can be directly obtained from cyclopentadiene, which is easily available.

RESULTS

Preparation and Properties of Polymers.—Typical conditions for synthesis of the polymers, their number average molecular weights, M_n, and reference designations of polymers are given in Table 1. These materials are brown-red powders with similar decomposition points and solubilities (see ref. 3). Analytical compositions of the polymers A—A_6, prepared without retarder, are given in Table 2. The molecular weights are not dependent on initial concentrations of monomer or catalyst or on degree of conversion. This has already been pointed out for polymer A, the earlier results [2] having been confirmed by vapour-phase osmometry. Typical results for two other polymers are given in Table 3. The suggested acid residues (line 11 of Table 2) are in accordance with the observed halogen content and alkali consumption. The bromine uptake, last line of Table 2, shows that these polymers are highly unsaturated.

[6] E. A. Guggenheim, *Phil. Mag.*, 1926, **7**, 538.

[7] Cf. I. M. Kolthoff and S. Bruckenstein, *J. Amer. Chem. Soc.*, 1956, **78**, 1.

TABLE 1

Preparation and molecular weights, M_n, of deeply coloured polymers from 3-(cyclopenta-2,4-dienyl)-cyclopentyl trichloroacetate, (I); solvent benzene, 20°

Acid	Proton acceptor	Initial concn. (mole/l.) (I)	Initial concn. (mole/l.) Acid	Initial concn. (mole/l.) Proton acceptor	Reaction time (hr.)	Yield, % of ester (I)	$10^{-3}M_n$	Ref. designation of polymer
Trichloroacetic	—	0·0230	0·300	—	115	>80	1·23 ± 0·12	A
Dichloroacetic	—	0·0970	2·90	—	72	35	1·73 ± 0·15	A_1
Acetic	—	0·0950	5·70	—	2100	20	1·02 ± 0·10	A_2
Hydrochloric	—	0·0870	0·440	—	48	35	1·28 ± 0·15	A_3
Trifluoroacetic	—	0·0970	1·20	—	7	35	1·46 ± 0·15	A_4
Monochloroacetic...	—	0·0970	1·00	—	240	20	1·23 ± 0·12	A_5
Diphenylphosphoric	—	0·100	1·00	—	82	20	0·975 ± 0·09	A_6
Trichloroacetic......	Acetone	0·0220	0·300	0·100	140	<15	0·68 ± 0·03	A_7
				0·200	146		0·58 ± 0·03	A_8
				0·300	160		0·55 ± 0·03	A_9
				0·400	134		0·49 ± 0·03	A_{10}
	Dioxan			0·200	184		0·65 ± 0·04	A_{11}
	Water		0·460	0·400	48		0·72 ± 0·06	A_{12}
	Ethanol		0·312	0·200	90		0·52 ± 0·04	A_{13}
	Piperidine		0·210	0·100	156		0·94 ± 0·08	A_{14}

Polymers A_7—A_{14}, prepared in the presence of retarders, were of similar unsaturation and contained 80·7—84·6% carbon, 7·6—8·2% hydrogen, and 0·15—0·5 trichloroacetate residues per mole of polymer. In experiments with retarders it is to be expected that the molecular weight of the polymers will depend on the degree of conversion, p, of monomer and on the ratio s [*i.e.*, concentration of retarder/concentration of ester (I)]. No attempt has been made to measure the influence of p as, in the presence of retarders, only initial rates of polymerisation were measured, but the influence of the ratio s has been tested with retarder acetone (see Table 1).

The electronic spectra of all the polymers are similar to those shown in Figure 2 of ref. 3, the deep colour being due to the tail end of a peak in the ultraviolet. The spectra of adducts containing, *e.g.*, polymer A and, respectively, trichloroacetic, dichloroacetic, trifluoroacetic, hydrochloric, or diphenylphosphoric acid, resemble each other. Typical positions of the peaks of electronic spectra and extinction coefficients, ε, are in ref. 3 and Table 4; ε is expressed in terms of mole polymer per litre not base mole per litre. The spectra of polymers A_7—A_{14} in 1M-solutions of trichloroacetic acid (solvent benzene) do not show peaks or shoulders at 480—490 mμ, but the other peaks were present.

Proton Acceptor Properties and Electrical Conductance.—Numerical values of the equilibrium constant, K, of reaction (1), relating to different catalysts and to polymer A, are given in Table 5.

TABLE 2

Analytical composition, alkali and bromine consumption, and suggested acid residues in deeply coloured polymers, prepared in absence of proton acceptors

Polymer	A	A_1	A_2	A_3	A_4	A_5	A_6
% C	81·2 ± 0·2	82·3 ± 0·3	77·7 ± 0·4	78·7 ± 0·3	80·9 ± 0·3	85·5 ± 0·3	85·7 ± 0·3
% H	7·91 ± 0·2	8·6 ± 0·3	7·6 ± 0·3	7·9 ± 0·3	7·9 ± 0·3	7·9 ± 0·3	8·1 ± 0·3
% Cl	7·60 ± 0·2	5·6 ± 0·2	9·4 ± 0·2	8·76 ± 0·2	1·1 ± 0·3	3·3 ± 0·2	<0·2
% F	—	—	—	—	4·1 ± 0·2	—	—
% P	—	—	—	—	—	—	<0·2
% O	3·3 ± 0·6	3·0 ± 0·8	5·3 ± 0·9	4·6 ± 0·8	4·6 ± 1·1	5·8 ± 0·8	6·2 ± 1
Equiv. per mole polymer Cl ...	2·6 ± 0·4	2·7 ± 0·3	2·7 ± 0·3	3·2 ± 0·3	<0·6	1·2 ± 0·2	<0·1
Equiv. per mole polymer F ...	—	—	—	—	3·1 ± 0·3	—	—
Equiv. per mole polymer P ...	—	—	—	—	—	—	<0·1
Equiv. alkali per mole polymer ...	1·0 ± 0·2	0·90 ± 0·1	1·1 ± 0·1	1·1 ± 0·2	1·2 ± 0·2	1·1 ± 0·1	—
Suggested acid residue	$O{\cdot}CO{\cdot}CCl_3$				$O{\cdot}CO{\cdot}CF_3$	$O{\cdot}CO{\cdot}CH_2Cl$	None
No. of C_5H_5 groups per mole polymer	16 ± 2	24 ± 2	13 ± 1	17 ± 2	19 ± 3	17 ± 2	15 ± 2
Equiv. Br per C_5H_5 residue	2·0 ± 0·3	2·0 ± 0·3	2·2 ± 0·3	2·4 ± 0·3	1·7 ± 0·4	2·2 ± 0·3	1·7 ± 0·3

TABLE 3

Molecular weights, M_n, of polymers prepared under different conditions. Solvent benzene 25·0°

Polymer	Initial concn. (mole/l.) (I)	Initial concn. (mole/l.) catalyst	% Ester (I) used up	M_n
A_3	0·200	0·440	>90	1280 ± 100
	0·0870	0·190		1330 ± 100
	0·0500	0·190		1230 ± 100
	0·0500	0·190	50	1245 ± 100
A_4	0·230	1·20	95	1510 ± 150
	0·0970	1·20	95	1460 ± 150
	0·0970	1·20	50	1360 ± 150
	0·0970	0·605	54	1515 ± 150

TABLE 4

Electronic spectra of ion-pairs from polymers and 1·00M-trichloroacetic acid in benzene at 20°. Polymer concentration $0·6 \times 10^{-3}$—$1·1 \times 10^{-3}$M

Polymer	($\lambda_{max.}$ mμ)	$10^{-3}\varepsilon_{max.}$ (l./mole cm.)	$\lambda_{1/2}$ (mμ)*
A_3	480, 540, 610	7·5, 7·5, 7·0	840
A_5	480sh, 530, 600	6·6, 6·6, 6·7	740
A_6	490, 540sh, 610	4·6, 5·7, 7·8	780

* Wavelength at which the molar light absorption coefficient, ε, is one half of $\varepsilon_{max.}$ in column 7.

TABLE 5

Equilibrium constants of proton transfer, *K*, relating to polymer A and different proton donors. Solvent benzene, 20°

Acid	Concn. (mole/l.) Acid	Concn. (mole/l.) Polymer (concn. × 10^4)	No. of tests	$\log_{10} K$ (K in l./mol.)
Trichloroacetic	0·0200—3·50	0·337—12·3	163	1·0 ± 0·1
Dichloroacetic	0·155—3·48	0·623—7·05	10	−0·19 ± 0·06
Acetic	1·75—12·3	0·800—3·79	7	−2·6 ± 0·5
Hydrochloric	0·0176—0·430	0·543—2·52	14	1·0 ± 0·2 *
Trifluoroacetic	0·0122—0·896	3·13	10	1·4 ± 0·1
Monochloroacetic	0·325—1·56	4·08—16·6	8	−1·2 ± 0·1
Diphenylphosphoric	0·0100—1·50	1·50	5	−0·4 ± 0·1

* This *K* value was determined with a vacuum light-absorption cell fitted with a tap (see p. 3254). In earlier [3] experiments with hydrochloric acid a less reliable technique was used.

All plots of log β (see equation 3) *vs.* the logarithm of the acid concentration were linear, of slope 1·0 ± 0·1. This is in accordance with the stoicheiometry of equation (1). When the precautions mentioned on page 3254 are adopted the accuracy of the equilibrium constants is as specified in the last column of Table 5. Within this experimental error, the *K* values relating to trichloroacetic acid, and to different polymers, agree with each other. Results of electrical conductance measurements of ion-pairs formed from polymers A—A_6 and trichloroacetic acid are in Table 6. The Λ and Λ_0 values in the fourth and fifth column are the molar electrical conductances at a specified ion-pair concentration, $c' = 10^{-3}$ mole/l., and at infinite dilution. The concentration c' was calculated from the stoicheiometric polymer concentration and the appropriate *K* values in Table 5. As the temperature coefficient of *K* is small (see ref. 3), it is permissible to disregard the difference between $K_{20°}$ and $K_{25°}$. The slope of the linear log Λ *vs.* log c' graphs is in most experiments 0·45 ± 0·05, in reasonable agreement with equation (4), from which the ion-pair dissociation constants, K_d, in the last column of Table 6, were calculated. The Λ, Λ_0, and K_d values of trichloroacetic acid adducts of polymers A_7—A_{14} (solvent benzene, 25·0°), and the corresponding parameter of Table 6 are similar. For polymers A_9, A_{11}, and A_{13}, for instance, $-\log K_d$ was, respectively, 5·6 ± 1, 5·4 ± 1·0, and 6·4 ± 1·0. Molar electrical conductances and ion-pair dissociation constants of the polymers do not depend on the concentration or nature of the acids. This follows from experiments with trichloro-, trifluoro-, and dichloro-acetic acids (0·112—3·00M), acetic acid (3·0—7·1M), hydrochloric acid (0·197—0·313M), and diphenylphosphoric acid (0·54M). In all these systems the K_d values

TABLE 6

Results of electrical-conductance measurements in benzene, 1·00M, with respect to trichloroacetic acid; 25·0°

For significance of symbols see text

c' and K_d in mole/l. Λ and Λ_0 in $1 \times \Omega^{-1}$ cm.$^{-1}$ mole^{-1}

Polymer	Range of $\log_{10} c'$	No. of tests	$-\log_{10} \Lambda$ ($c' = 10^{-3}$)	$-\log_{10} \Lambda_0$	$-\log_{10} K_d$
A	2·0—4·3	15	5·20 ± 0·10	3·0 ± 0·5	6·8 ± 1·0
A_1	2·7—5·5	5	4·90 ± 0·20	3·0 ± 0·5	6·8 ± 1·0
A_2	2·6—4·3	4	5·35 ± 0·20	3·5 ± 0·5	6·8 ± 1·0
A_3	2·6—5·2	5	5·20 ± 0·10	3·4 ± 0·5	6·6 ± 1·5
A_4	2·8—5·3	5	5·45 ± 0·20	4·0 ± 0·5	5·0 ± 1·5
A_5	3·2—5·2	5	5·30 ± 0·20	3·5 ± 0·5	5·0 ± 1·5
A_6	2·9—5·5	5	5·30 ± 0·20	3·5 ± 0·5	6·0 ± 1·5

TABLE 7

Rates of polymerisation of ester (I), benzene 25·0°; typical results derived from electrical-conductance measurements

a				*b*		
Time (min.)		$10^{-6}\Omega$	$10^6 c$	Time (min.)	$10^{-6}\Omega$	$10^6 c$
10	t	50·0	66·0	10	167	65
20		35·0	121	20	105	120
30		29·6	175	30	83·4	170
40		25·0	220	40	70·2	230
50		22·8	255	50	62·6	280
60		21·0	288	60	56·4	330
210	τ	15·7	498	80	47·0	460
220		15·65	500	100	40·8	600
230		15·6	502	120	36·0	740
240		15·55	504	150	30·8	950
250		15·5	506			
260		14·45	308			

(*a*) 0·448M in trifluoroacetic acid; initial concentration, c_o, of ester (I) = 0·0175 M; no retarder; cell constant 0·166 cm.$^{-1}$; (*b*) 0·312M in trichloroacetic acid and 0·412M in retarder acetone; c_o of ester (I) = 0·0446M; cell constant 0·153 cm.$^{-1}$. The Ω-values are the observed resistances in ohms; the *c*-values are polymer concentrations in mole/l., derived from Ω with the help of the calibration graphs shown in Figure 4. Times *t* and τ relate to the calculation of velocity constants (see below).

TABLE 8

Velocity coefficients of conversion of ester (I) into deeply coloured polymers without retarder; benzene solution, 25·0°

Acid	Polymer formed	Initial concn. (mole/l.)		No. of tests	% Conversion	$10^2 k$ (l./mole-min.)	Experimental technique*
		Acid	(I)				
$Cl_3C{\cdot}CO_2H$ ...	A	0·0800—1·000	0·00500—0·950	18	10—80	1·5 ± 0·2	1 and 2
		0·312	0·0209	2	33—50	1·6 ± 0·1	3
$Cl_2HC{\cdot}CO_2H$	A_1	0·444—0·879	0·0185—0·0740	10	25—80	0·40 ± 0·05	3
$CH_3{\cdot}CO_2H$ ...	A_2	3·13—6·11	0·0266	2	2—4	~0·0001	4
HCl	A_3	0·0417—0·357	0·00638—0·0548	8	10—62	2·2 ± 0·4	1
$CF_3{\cdot}CO_2H$ ...	A_4	0·112—0·448	0·00585—0·0112	12	13—42	3·4 ± 0·3	3
$ClH_2C{\cdot}CO_2H$	A_5	0·372—0·744	0·0366—0·155	6	5—11	0·028 ± 0·003	4
Diphenyl-phosphoric	A_6	0·270—0·540	0·0134—0·0894	8	1—4	0·037 ± 0·004	4

1, Optical density measurements (see ref. 2); 2, titration of liberated acid (see ref. 2); 3, electrical conductivity measurements (Guggenheim plots); 4, electrical conductivity measurements (initial rate, see text).

were calculated from equation (4), although the experiments with polymer A_1 and dichloroacetic acid, polymer A_2 and acetic acid, polymer A_4 and trifluoroacetic acid, and polymer A_5 and monochloroacetic acid showed that the slope of the linear log Λ *vs.* log c' plots were somewhat smaller than 0·50, namely 0·40 ± 0·04 (a possible explanation for this will be given elsewhere.) All the ion-pair dissociation constants, K_d, relate to binary ion-pairs, not to higher aggregates, which may play a role if the polymer concentrations are higher. The specified accuracy of the molar electrical conductances at infinite dilution and of the ion-pair dissociation constants is low, but it is sufficient to show that the K_d values are several order of magnitude larger than those relating to ion-pairs in which the positive charge of the cation is not spread

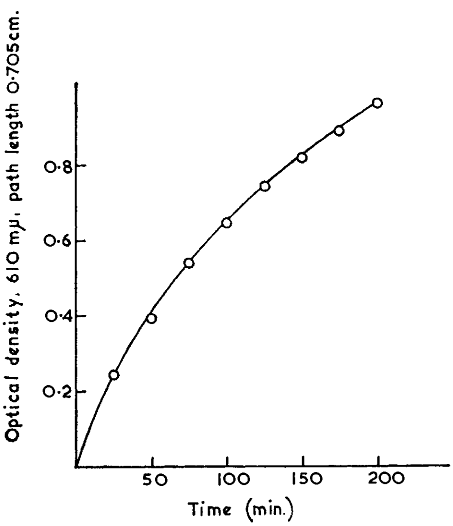

FIGURE 5. Rate of polymerisation of ester (I), under catalysis by hydrochloric acid; benzene, 25·0°; typical optical-density tests. Initial concentration ester (I) = 0·00947M; concentration HCl = 0·351M

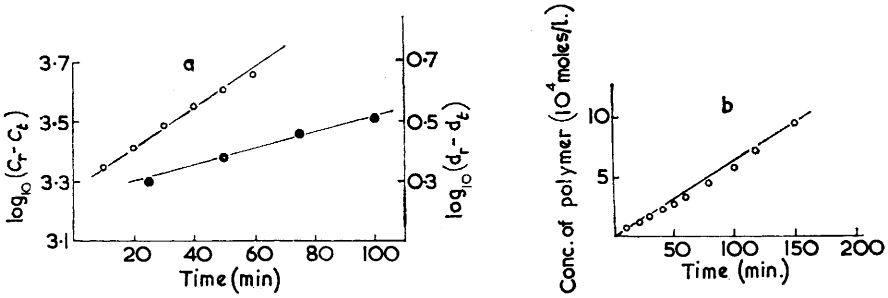

FIGURE 6. Evaluation of rate coefficients of polymerisation of ester (I), in benzene, 25·0°, from results of electrical conductance and optical-density measurements

(a) Typical Guggenheim plots. ○ (left ordinate, conductance tests); initial concentrations (mole/l.); trifluoroacetic acid = 0·448; ester (I) = 0·0175; c_τ and c_t are the concentrations of polymer at times τ and t. ● (right ordinate, optical-density measurements); initial concentrations (mole/l.); hydrochloric acid = 0·351; ester (I) = 0·00947; d_τ and d_t are optical densities (610 mμ, 0·705 cm. path length) at times τ and t

Multiplying the slopes of these graphs by 2·30 and dividing by the acid concentration gives the velocity constant, k, defined by equation (6)

(b) Typical graph showing the initial rate of polymerisation (deduced from conductances): concentration (mole/l.): trichloroacetic acid = 0·312; ester (I) = 0·0446; acetone = 0·412. Multiplying the slope of the graph by the average degree of polymerisation, n, derived from the molecular weight in the eleventh line of Table 1, and dividing by the concentration of ester (I), gives the velocity constant, k', defined by equation (5)

over a sequence of conjugated double bonds (see ref. 3). Further evidence for the presence of conjugated double bonds in these polymers are the electronic spectra and the proton acceptor properties.

Kinetics of Polymerisation.—Typical details of rate measurements and the results of kinetic tests without retarders are in Tables 7 and 8 and in Figures 5 and 6. These catalysed polymerisations are of the first order with respect to ester (I) because linear Guggenheim plots were

TABLE 9

Kinetics of trichloroacetic acid-catalysed polymerisation of ester (I) in presence of proton acceptor acetone; benzene solution, 25·0°. k_ρ and k_ρ^F in l./mole min.

	Initial concn. (mole/l.)							
		Acid						
Ref.	Acetone	Stoicheiometric	Free	(I)	10^3k_ρ	$\frac{10^2k_\rho}{[(I)]}$	$10^2k_\rho^F$	% Retardation (ρ)
1	0·412	0·312	0·0270	0·0223	1·7 ± 0·2	7·6 ± 0·6	2·0 ± 0·3	>80
2	0·412	0·312	0·0270	0·0446	1·8 ± 0·2	4·0 ± 0·4	2·1 ± 0·3	
3	0·412	0·312	0·0270	0·0892	2·0 ± 0·2	2·2 ± 0·2	2·3 ± 0·3	
4	0·412	0·312	0·0270	0·178	2·2 ± 0·2	1·2 ± 0·1	2·5 ± 0·3	
5	0·103	0·312	0·200	0·0113	12 ± 1·5	106 ± 10	1·9 ± 0·3	20 ± 10
6	0·103	0·312	0·200	0·0223	12 ± 1·5	54 ± 5	1·9 ± 0·3	
7	0·103	0·312	0·200	0·0450	15 ± 1·5	33 ± 3	2·3 ± 0·3	
8	0·103	0·150	0·0480	0·0223	5·8 ± 0·7	—	1·8 ± 0·3	65 ± 10
9	0·103	0·600	0·333	0·0223	13 ± 2	—	2·3 ± 0·3	13 ± 8
10	0·206	0·312	0·0800	0·0223	3·8 ± 0·4	—	1·5 ± 0·2	75 ± 10
11	0·308	0·312	0·0500	0·0223	2·4 ± 0·3	—	1·5 ± 0·2 k_ρ^F	>80

TABLE 10

Retardation of trichloroacetic acid-catalysed polymerisation of ester (I) by proton acceptors; benzene solution, 25·0°

	Initial concn. (mole/l.)				
		Acid			
Proton acceptor	Proton acceptor	Stoicheiometric	Free	(I)	% Retardation (ρ)
Dioxan	0·103—0·200	0·312	0·0220—0·0500	0·0223—0·0994	>80
Water	0·200—0·500	0·458	0·0200—0·0600	0·0100	>70
Ethanol............	0·100—0·205	0·312	0·0300—0·0900	0·0209	>50
Piperidine.........	0·0500—0·100	0·312	0·0230—0·0850	0·0209	>50

obtained and because there was no significant trend of velocity constants in runs in which the initial concentrations were varied within the range given in columns 3 and 4 of Table 8. The results of rate measurements carried out with retarder acetone are in Table 9. The concentration of free acid (column 4) was calculated from results of measurements shown in Figure 7, or from similar results using equation (10). The velocity constants k_ρ and k_ρ^F are

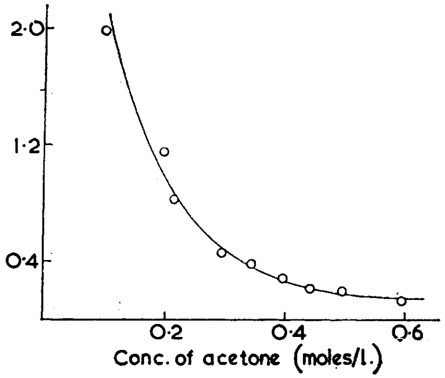

FIGURE 7. Influence of acetone concentration on β_ρ, defined by equation (9). Reaction mixture $1·04 \times 10^{-4}$M in polymer A and $1·00 \times 10^{-5}$M with respect to α-tocopherol. Stoicheiometric concentration of trichloroacetic acid 0·312M. Solvent benzene, 20°; the optical densities were determined with light of 610 mμ.

defined by equations (7) and (8). For reasons discussed below, it is of interest to list also some ratios $k_\rho/[(I)]$; these are in column 7 of Table 9. The ρ-values in the last column of Tables 9 and 10 are percentage retardation calculated from $100(k - k_\rho)/k$, where the velocity constant, k, was taken from Table 8, first line. The rate of polymerisation of ester (I) was also measured in the presence of the retarders listed in the first column of Table 10. In these experiments, the k_p values were in the range 1×10^{-3}—9×10^{-3} l./mol. min., whilst k_p^F was between 2×10^{-2} and 4×10^{-2} l./mol. min.

DISCUSSION

Experiments without Retarders.—The analytical results (Table 2) show that the stoicheiometry of these polymerisations depends on the acid catalyst and that there are three modes of reaction *

$$n\mathrm{C_{10}H_{13}B} \xrightarrow{\mathrm{HB}_c} \mathrm{R}_n\mathrm{B} + (n - 1)\mathrm{HB} \qquad (11)$$

$$n\mathrm{C_{10}H_{13}B} \xrightarrow{\mathrm{HB}_c} \mathrm{R}_n\mathrm{B}_c + n\mathrm{HB} \qquad (12)$$

$$n\mathrm{C_{10}H_{13}B} \xrightarrow{\mathrm{HB}_c} \mathrm{R}_n + n\mathrm{HB} \qquad (13)$$

The symbols n, $\mathrm{C_{10}H_{13}B}$, HB_c, and R indicate, respectively, the number average degree of polymerisation, ester (I), the catalyst, and $\mathrm{C_{10}}$-residues in the polymer.† Reaction (11) applies to the formation of those polymers, A—$\mathrm{A_3}$, which contain the same acid residue, B, as ester (I), reaction (12) represents the synthesis of polymers $\mathrm{A_4}$ and $\mathrm{A_5}$ which contain an acid residue B_c different from that in ester (I) and identical with that of the relevant catalyst, and reaction (13) is appropriate to the conversion into polymer $\mathrm{A_6}$, which is not an ester. All the polymers, however, contain about one double bond per $\mathrm{C_5}$-unit (see last line of Table 2) and the electronic spectra, proton acceptor properties, and electrical conductances (Tables 4—6) show that some of the double bonds are conjugated. The type of hydrogen migration conducive to formation of conjugated double bonds in reaction (11) has been discussed.[2] A similar rationalisation can be carried out for the other stoicheiometric types (12) or (13) as shown below.

These polymerisations are stoicheiometrically polycondensations, but from a mechanistic point of view they are addition polymerisations. This follows from the observed molecular-weight relationships and kinetics, which are consistent with a relatively slow initiation, involving proton uptake by ester (I) and propagation and termination steps in which ester (I) reacts with growing carbonium-ion pairs. These steps are represented by

$$\text{Initiation} \left\{ \begin{array}{l} \text{Reaction (11): } \mathrm{C_{10}H_{13}B} + \mathrm{HB}_c \xrightarrow{k_i} (\mathrm{RB})^+ \cdots \mathrm{B}_c^+ \\ \\ \text{Reaction (12) and (13) } \mathrm{C_{10}H_{13}B} + \mathrm{HB}_c \xrightarrow{k_i} \mathrm{R}^+ \cdots \mathrm{B}_c^- + \mathrm{HB} \end{array} \right. \qquad (14)$$

$$\text{Propagation} \left\{ \begin{array}{l} \text{Reaction (11): } (\mathrm{R}_r\mathrm{B})^+ \cdots \mathrm{B}_c^- + \mathrm{C_{10}H_{13}B} \xrightarrow{k_p} (\mathrm{R}_{r+1}\mathrm{B})^+ \cdots \mathrm{B}_c^- + \mathrm{HB} \\ \\ \text{Reaction (12) and (13) } \mathrm{R}_r^+ \cdots \mathrm{B}_c^- + \mathrm{C_{10}H_{13}B} \xrightarrow{k_p} \mathrm{R}_{r+1}^+ \cdots \mathrm{B}_c^- + \mathrm{HB} \end{array} \right. \qquad (15)$$

$$\text{Termination} \left\{ \begin{array}{l} \text{Reaction (11): } (\mathrm{R}_r\mathrm{B})^+ \cdots \mathrm{B}_c^- + \mathrm{C_{10}H_{13}B} \xrightarrow{k_t} \mathrm{R}_{r+1}\mathrm{B} + \mathrm{HB} + \mathrm{HB}_c \\ \text{Reaction (12): } \mathrm{R}_r^+ \cdots \mathrm{B}_c^- + \mathrm{C_{10}H_{13}B} \xrightarrow{k_t} \mathrm{R}_{r+1}\mathrm{B}_c + \mathrm{HB} \\ \text{Reaction (13): } \mathrm{R}_r^+ \cdots \mathrm{B}_c^- + \mathrm{C_{10}H_{13}B} \xrightarrow{k_t} \mathrm{R}_{r+1} + \mathrm{HB} + \mathrm{HB}_c \end{array} \right. \qquad (16)$$

where k_i, k_p, and k_t are rate constants, $(\mathrm{RB})^+ \cdots \mathrm{B}_c^-$, $\mathrm{R}^+ \cdots \mathrm{B}_c^-$, $(\mathrm{R}_{r+1}\,\mathrm{B})^+ \cdots \mathrm{B}_c^-$, $\mathrm{R}_{r+1}^+ \cdots \mathrm{B}_c^-$ are growing carbonium-ion pairs, r is the number of repeat units, 1, 2, 3,. . ., $\mathrm{R}_{r+1}\mathrm{B}$, $\mathrm{R}_{r+1}\mathrm{B}_c$, and R_{r+1} are deprotonated dead polymers.‡ It had been suggested [2] that

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* Reactions (11)—(13), and (16) describe situations in which the acid concentration is so low that the equilibrium (1) is shifted far towards the left hand side; in equilibrium (1) the deprotonated polymers are designated as P, for the sake of brevity.

† The number of hydrogen atoms per residue R need not be specified.

‡ Protonated dead polymers PH^+ [see equilibrium (1)] should be designated in the symbolism of (16) by $\mathrm{R}_{r+1}{}^+\mathrm{HB}$, $\mathrm{R}_{r+1}{}^+\mathrm{HB}_c$, $(\mathrm{R}_{r+1}{}^+\mathrm{H})$; they are different from growing carbonium ions (see ref. 2).

in the propagation steps (15) the monomer reacts with a carbon atom which is joined to three other carbons, while in the termination steps (16) a carbon atom is involved which is joined to two other carbons and one hydrogen. Only the latter reaction can lead to deprotonation and formation of a sequence of conjugated double bonds, thereby stabilising the resulting species sufficiently to terminate further growth. This hypothesis is reasonable because it is accepted that conjugated double bonds can have a stabilising influence and because the electronic spectra, proton acceptor properties, and electrical conductances of the dead polymers prove that a sequence of conjugated double bonds is formed.

The expressions for the rate of polymerisation, $-d[(I)]/dt$, and the number average degree of polymerisation, n, derived from (14), (15), and (16), with the help of previously [2] specified assumptions, are

$$-\frac{d[(I)]}{dt} = \left\{2k_i + \frac{k_i k_p}{k_t}\right\}[(I)][HB] \qquad (17)$$

$$n = (k_p/k_t) + 2 \qquad (18)$$

The observed common rate law of these polymerisations [first-order with respect to ester (I) and acid] and the observed independence of the molecular weights on concentration conditions are correctly described by these equations.

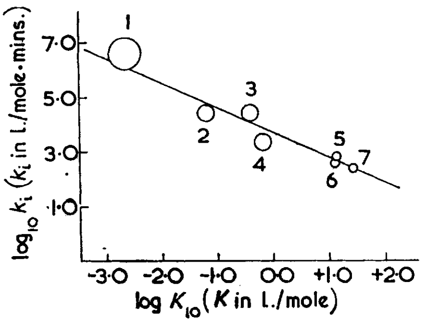
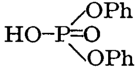


FIGURE 8. Linear functional relationship between equilibrium constants of proton transfer, K, taken from Table 5 and rate constants, k_i relating to the initiation of polymerisation. The catalysts to which the K and k_i values relate are indicated by numbers

1, $CH_3 \cdot CO_2H$
2, $ClCH_2 \cdot CO_2H$
3, 
$HO{-}P({=}O)(OPh)_2$
4, $Cl_2H \cdot C \cdot CO_2H$
5, $Cl_3C \cdot CO_2H$
6, HCl
7, $F_3C \cdot CO_2H$

The diameters of the circles indicate, approximately, the relative experimental errors

Velocity constants k_i, relating to the initiation steps (14), are obtained from rate equation (17) and the ratios k_p/k_t deduced from the observed degrees of polymerisation. Figure 8 shows an approximately linear relationship between the logarithm of the velocity constants, k_i, and the logarithm of the equilibrium constants of proton transfer, K, in Table 5. This type of Brönsted correlation is characteristic of authentic proton transfer reactions in aprotic solvents.[8] It could not be expected to hold in the present case if the important assumption, that the initiation step of these polymerisations are relatively slow proton transfer processes, were not justified.

An unusual feature of the proposed mechanism is the second-order termination, involving ester (I) as a participant. A first-order termination, *e.g.*, due to release of acid or to a collapse of a growing carbonium-ion pair, is more plausible, at least for systems in which formation of conjugated double bonds plays no role. At any rate, however, a first-order termination, together with a relatively slow second-order initiation and a second-order propagation,* should make the overall rate of polymerisation of the second order with respect to ester (I), and moreover the number average degree of polymerisation should increase with increasing concentration of ester (I). This has not been observed.

Transfer reactions involving solvent or polymer play no significant role under the

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[8] See, *e.g.*, R. P. Bell, " Acid-Base Catalysis," Oxford University Press, Oxford, 1941.

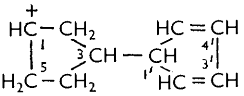
* The possibility that the propagation steps of these reactions involving growing species of seven different types are zero order with respect to monomer is not considered here.

conditions of these experiments because the degree of polymerisation, n, is not influenced by concentration changes, addition of dead polymer,[2] or by change of solvent.[2] It could be suggested that termination by monomer is less probable than transfer to monomer, *e.g.*,

$$(R_rB)^+ \cdots B_c^- + C_{10}H_{13}B \longrightarrow R_rB + (RB)^+ \cdots B_c^- \qquad (19)$$

Reactions of this type, although compatible with the observed rate and molecular-weight relationships, are not taken into account because the previously discussed structural aspects[2] relating to formation of conjugated double bonds require incorporation of monomer in accordance with termination steps (16). At any rate, however, the principal feature of the suggested mechanism, that the initiation step is a relatively slow proton transfer reaction, is not affected by the possible occurrence of reaction (19) or a similar monomer transfer reaction.

Structural Aspects.—To account for the stoicheiometry of reactions (12) or (13) it is assumed that trichloroacetic acid is released in the initiation step of the polymerisation, thereby producing a transient species of formula



An isomer, of formula similar to that designated by A on page 1972 of ref. 2, can be obtained by hydrogen shift from positions 2 to 1, 3 to 2′, and 1′ to 3′. Most structural aspects of reactions (12) and (13) can be rationalised, therefore, by a formalism similar to that described in ref. 2. To account for the observation that polymers A_4 and A_5 contain acid residues identical with those derived from the catalysts, but different from the acid residue in ester (I), and that the overall rate law is nevertheless unchanged, it is suggested that the termination is the result of two consecutive reactions. The first slow one involves reaction with ester (I), while the other process, not rate-determining, is a collapse of a growing carbonium-ion pair. It is not claimed that these considerations or the structural aspects discussed in ref. 2 are a unique explanation of the observed effects.

Retardation by Proton Acceptors.—This is further evidence for the importance of proton transfer reactions in these polymerisations. The chlorine analyses of polymers A_7—A_{14} show that a fractional number (0·15—0·5) of trichloroacetate residues are incorporated in one mole of these materials. It is probable, therefore, that in presence of retarders, reactions of type (11) or (12) and (13) occur simultaneously. Other analytical data and the spectrophotometric and electrical conductance tests show that these polymers are highly unsaturated and contain some conjugated double bonds, the incipient formation of which may stabilise transition states conducive to terminations of type (16). The figures in column 8 of Table 1 (last 8 lines) show, however, that the molecular weights of polymers A_7—A_{14}, which were prepared in the presence of retarders, are relatively low. In order to explain this, it is suggested that additional termination steps occur, namely

$$x(R_rB)^+ \cdots B_c^- + Q \xrightarrow{k_{t'}} R_rB + Q \cdots (H^+ \cdots B_c^-)_x \qquad (20)$$

$$x(R_r)^+ \cdots B_c^- + Q \xrightarrow{k_{t'}} R_r + Q \cdots (H^+ \cdots B_c^-)_x \qquad (21)$$

where x is the number of basic sites in the retarder, Q, $(R_rB)^+ \cdots B_c^-$ etc. have the same significance as in equations (16), $k_{t'}$ is the rate constant and $Q \cdots (H^+ \cdots B_c^+)_x$ is a retarder catalyst adduct. In the case of retarder acetone, it is reasonable to assume that x of equations (20) or (21) is unity, and this base has been selected for a more careful study. If termination by ester (I) and acetone occurs simultaneously, a treatment, similar to that mentioned in the preceding section, gives

$$-\frac{d[(I)]}{dt} = \left\{k_i + \frac{k_i(k_t + k_p)[(I)]}{k_t[(I)] + k_{t'}[Ac]}\right\}[(I)][HB] \qquad (22)$$

$$\frac{1}{n} = \frac{k_t}{k_p} + \left\{\frac{k_{t'}}{k_p[(I)]}\right\}[Ac] \qquad (23)$$

where $k_{t'}$ is the rate constant of reaction (20) or (21), [Ac] is the stoicheiometric acetone concentration, and the other symbols have the same significance as in equations (17) and (18). Figure 9 shows the functional relationship between the reciprocal degrees of polymerisation and the acetone concentration. The intercept and the slope of the straight line are interpreted as k_t/k_p and $k_{t'}/k_p[(I)]$; and it can be deduced from the numerical values that $k_t/k_{t'} = 30 \pm 8$ at the specified concentration of ester (I) and temperature. If, therefore, the concentrations of ester (I) and acetone are in the range given in Table 9, the two terms $k_t[(I)]$ and $k_{t'}[Ac]$ in equation (22) should be of the same order of magnitude. Under these conditions the rate of the retarded polymerisation should be neither first nor second-order with respect to ester (I), a conclusion confirmed by the trend of the velocity constants k_ρ and the ratios $k_\rho/[(I)]$, refs. 1—4 in Table 9. At the highest concentration of ester (I), however, one can neglect $k_{t'}[Ac]$ in equation (22), as a first approximation, so that in this case the retardation should be relatively small. This is at variance with the observed retardation, ref. 4 in Table 9, which is over 80%. It is probable, therefore, that another effect plays a role, namely a decrease of the effective catalyst concentration owing to the formation of a trichloroacetic acid–retarder adduct in a pre-equilibrium. This appears to be rapidly established because the sequence of mixing monomer, retarder, and catalyst (see p. 3255) had no detectable effect on the rate of polymerisation. In the experiments with acetone the rate should be given by

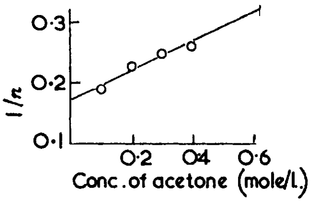


FIGURE 9. Influence of acetone concentration on reciprocal degree of polymerisation, calculated from the molecular weights in lines 8—11 of Table 1. Intercept = 0·16 ± 0·02; slope = 0·25 ± 0·05 l./mole; initial concentration of ester(I) = $2{\cdot}20 \times 10^{-2}$ mole/l.

$$-\frac{d[(I)]}{dt} \approx \left(2k_i + \frac{k_i k_p}{k_t}\right)[(I)][HB]_F \qquad (24)$$

where the concentration of the free acid, $[HB]_F$ is defined by equation (10), it being again assumed, as a first approximation, that $k_{t'}$ [Ac] in equation (22) can be neglected. Comparison of equations (24) and (17) indicates that the overall rate constant, k, of the unretarded polymerisation and the rate constants, k_ρ^F, defined by equation (8) should be of the same order. The figures in the first line of Table 8, column 7, and in Table 9, column 8 ref. 4, show that this is the case.

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