# 377. *Mechanism of Formation of a Deeply Coloured Electrically Conducting Polymer.*

By J. Murphy, L. Roubinek, and A. Wassermann.

3-(Cyclopenta-2,4-dienyl)cyclopentyl trichloroacetate (I) can be converted into the same polymer (A) as is obtained from cyclopentadiene. This is due to the occurrence of two consecutive reactions, the first leading from cyclopentadiene to the ester (I), and the second, slower reaction, giving polymer (A). A kinetic investigation of this polymerisation has been carried out and the degree ($n$) of polymerisation under different conditions determined. The results are compatible with proton-transfer in the initiation and incorporation of the ester (I) into growing carbonium-ion pairs during propagation and termination. It is suggested that all steps involve hydrogen shifts and that propagation and termination are accompanied by elimination of trichloroacetic acid. This mechanism accounts for the observed kinetics and $n$ values, and for the formation of non-linear species containing a short and a long sequence of conjugated double bonds.

The preceding paper[1] describes trichloroacetic acid-catalysed reactions of substances containing endocyclic double bonds in five-membered rings, which lead to deeply coloured polymers of unusual properties. An attempt is now made to elucidate the mechanism of one of these polymerisations. The formation of one polymer, termed (A),[1] was selected for study because the starting material, cyclopentadiene, is easily available and because this polymer has been more extensively investigated than the other products.

This paper deals with the stoicheiometry of the polymerisation which is formally, but not kinetically, a polycondensation, with the degree and rate of polymerisation, and with oxidative degradation. A detail of general interest is a method of calculus used for solution of a differential rate equation relating to two consecutive reactions.

## Experimental

The preparation of 3-(cyclopenta-2,4-dienyl)cyclopentyltrichloroacetate (I), the purification of trichloroacetic acid, cyclopentadiene, solvents, and added substances, removal of traces of peroxides, optical density measurements in absence of atmospheric oxygen, electrical conductance measurements and electrometric titrations have been described elsewhere.[1-6] Spectrophotometric and conductometric measurements showed that the ester (I) contained less than 2% of polymer (A). The equivalent weight of the ester was always somewhat lower than the theoretical value, owing to the presence of free acid, probably trichloroacetic acid (cf. below). The term $N_E$ in equation (5) (below) is the sum of the number of moles of ester (I) and of free acid. In measuring the rate of polymerisation of ester (I), by titrating liberated trichloroacetic acid, a correction was made for the free acid present in the ester at the start of the run. Titrations of liberated acid were carried out in benzene–ethanol or carbon tetrachloride–ethanol with indicators,[2-4,6] or electrometrically [1,6] if the solution was intensely coloured. In most experiments alcoholic potassium hydroxide was used, an excess of alkali being avoided. Control experiments with isopentylamine in benzene showed that the unused ester was not thus hydrolysed. Back-titrations were carried out with trichloroacetic acid in benzene.

In one set of measurements, a mixture was made of (*a*) the ester (I), previously shaken with barium oxide for several days, (*b*) benzene previously refluxed with potassium, and (*c*)

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[1] French, Roubinek, and Wassermann, preceding paper.

[2] Blakely, Gillespie, Roubinek, Wassermann, and White, *J.*, 1961 1939.

[3] Blakely, Ph.D. Thesis, London, 1957.

[4] French, Ph.D. Thesis, London, 1958.

[5] Wassermann, *J.*, 1954, 4329; 1959, 986.

[6] Roubinek, Ph.D. Thesis, London, 1960.

trichloroacetic acid, prepared from a film *in vacuo* [5] and dried for several hours at 40°/1 mm. over phosphorus pentoxide. This mixture was made in absence of atmospheric moisture, greaseless taps [1] being used, and the solution was filled into dry glass vessels; these were sealed off *in vacuo* and introduced into a thermostat bath. The rate coefficients obtained agreed to within the experimental error ($\pm 10\%$) with those determined in runs carried out in presence of atmospheric moisture. Solutions did not come into contact with taps coated with sugar grease,[1] because this retards the rate of polymerisation. In connexion with rate coefficients deduced from optical-density measurements, some experiments were done in which the optical cell [7] was sealed *in vacuo* and placed into a double-walled thermostat housing which fitted into the cell compartment of a Unicam S.P. 500 spectrophotometer.

The electronic spectra and specific electrical conductance, $\kappa$, of two sets of benzene solutions were determined: (*a*) final reaction mixtures obtained from ester (I) and trichloroacetic acid; (*b*) solutions containing known quantities of trichloroacetic acid and polymer (A), which had been purified as described before.[1] The positions of the light-absorption peaks,[8] optical densities and $\kappa$ values agreed to within the limits of experimental error ($\pm 5\%$) if the concentrations of solutions (*b*) were adjusted so that they coincided with those of solutions (*a*) on the assumption that there had been 100% conversion of starting material into polymer (A).

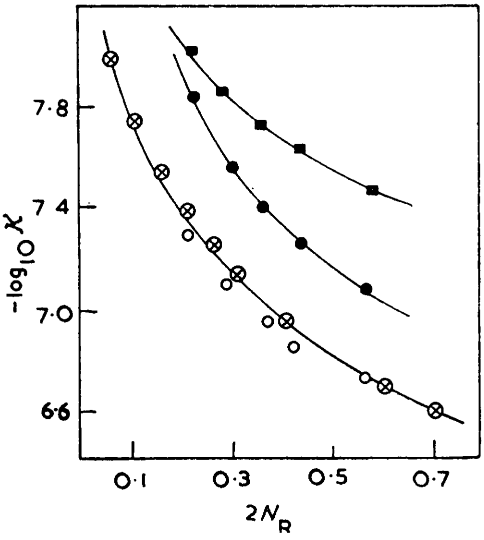

FIG. 1. *Relations between specific electrical conductance, $\kappa$ (in ohm$^{-1}$ cm.$^{-1}$), and $2N_R$ (for definition of $N_R$ see text); benzene solution at 25°.* $[CCl_3 \cdot CO_2H]$ = ■ 0·250, ● 0·500, ⊗ 1·50, ○ 2·00 *mole l.$^{-1}$.*

Conversion of ester (I) into polymer (A) under catalysis by trichloroacetic acid is accompanied by a gradual increase of the specific electrical conductivity, $\kappa$, until the limiting value [1] corresponding to complete polymerisation is reached. Fig. 1 shows the relation between log $\kappa$ and $N'_R$, the number of $C_{10}$ residues per l. of solution incorporated in polymer (A). Separate experiments with fractionated polymers of number-average molecular weight, $M_n$, in the range 844—1635 showed that the log $\kappa$–$N'_R$ relations are independent of $M_n$, within an accuracy of about 10%.

## RESULTS

*Stoicheiometry.*—The bimolecular dimerisation of cyclopentadiene occurs at 25° simultaneously with the catalysed dimerisation [9] if the reaction mixture contains $>0{\cdot}2$M-trichloroacetic acid. If the acid concentration is higher, *e.g.*, 0·5M, both the bimolecular and the catalysed dimerisation are overshadowed by a reaction leading to ester (I).[2,10] This ester, however, could only be isolated [2] if the reaction time was relatively short: after longer times,

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[7] Fig. 1 of ref. 1.
[8] Fig. 3 of ref. 1.
[9] Rubin, Steiner, and Wassermann, *J.*, 1949, 3046.
[10] Blakely and Wassermann, *J.*, 1961, 1946.

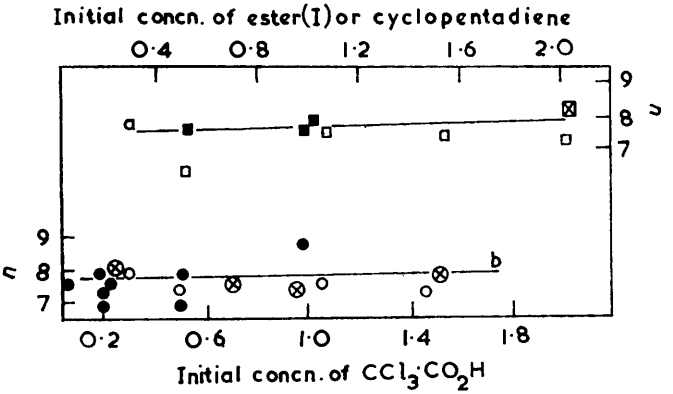
polymer (A) was the major product.[1] These observations indicate that the following two consecutive reactions occur:

$$2C_5H_6 + HB \xrightarrow{HB} C_{10}H_{13}B \quad \ldots \quad (1)$$

$$nC_{10}H_{13}B \xrightarrow{HB} R_nB + (n-1)HB \quad \ldots \quad (2)$$

where HB, $C_{10}H_{13}B$, R, and B are respectively symbols for trichloroacetic acid, ester (I), $C_{10}$ and trichloroacetate residues incorporated into polymer (A). Trichloroacetic acid is a reactant in (1), a product in (2), and a catalyst in both processes; the mechanism of the catalysis of reaction (1) has already been discussed,[10] and that of (2) will be dealt with below. Many experiments confirmed that the same polymer (A) is obtained from cyclopentadiene as from isolated ester (I), as established by the analytical composition, unsaturation, molecular and equivalent weight, electronic spectrum, and electrical conductance of the products. The results of one set of such experiments are in Fig. 2. A typical run in which polymer (A) was prepared from the isolated ester (I) was as follows: a dry benzene solution, 0·51M with respect to ester (I), 0·203M with respect to trichloroacetic acid, and about $10^{-3}$M with respect to the antioxidant α-tocopherol, was left for 23 hr. at 25°; then the deep blue solution was shaken with an excess of solid potassium hydrogen carbonate to remove free acid. After filtration, polymer (A) was isolated as described before;[1] the yield was over 90%.

FIG. 2. *Number-average degree of polymerisation, n, of polymer* (A); *benzene solution at* 25°.



*Influence of initial concentrations* (mole $l.^{-1}$) *of ester* (I) *or cyclopentadiene* (*upper abscissæ*) *and trichloroacetic acid* (*lower abscissæ*).

□ ■ ☒ *relate to upper abscissæ and right-hand ordinate.* [*In these experiments the initial concentration of cyclopentadiene or of ester* (I) *was varied.*]

○ ⊗ ● *relate to lower abscissæ and left-hand ordinate.* [*In these experiments the initial concentration of trichloroacetic acid was varied.*]

■ *and* ●: *Conversion of isolated ester* (I) *into polymer* (A) *in presence of air. Initial concn.*: *trichloroacetic acid,* 0·198—0·205M *for* ■; *ester* (I) 0·388—0·477M *for* ●.

□, ☒, ○, *and* ⊗: *Conversion of cyclopentadiene into polymer* (A) *without isolation of ester* (I). □ *and* ○, *In presence of air*; ☒ *and* ⊗, *in absence of air. Initial concn.*: *trichloroacetic acid,* 0·994—1·04M *for* □ *and* ☒; *cyclopentadiene* 0·921—1·10M *for* ○ *and* ⊗.

*Number-average Degree of Polymerisation, n, of Polymer* (A).—This is defined by:

$$n = (M_n - 163{\cdot}4)/132{\cdot}1 \quad \ldots \quad (3)$$

where $M_n$ is the number-average molecular weight. Polymer (A) is an ester of trichloroacetic acid,[1] the number-average equivalent weight of which equals $M_n$;[1] thus $n$ can be calculated from

$$n = N_R^{\infty}/(N_A^{\circ} - N_A^{\infty}) \quad \ldots \quad (4)$$

$$n = N_R^{\infty}/(N_E^{\circ} + N_A^{\circ} - N_A^{\infty}) \quad \ldots \quad (5)$$

where $N_R$, $N_E$, and $N_A$ are the number of moles per kg. of solution of, respectively, $C_{10}$ residues incorporated in the polymer, trichloroacetate in ester (I) (corrected for initial free acid), and trichloroacetic acid. The superscripts $^\circ$ and $^\infty$ indicate that the relevant quantities relate to zero time or to the end of polymerisation; equations (4) and (5) were applied to results of experiments in which the starting material was, respectively, cyclopentadiene and ester (I). $N_R$ was assumed to equal $\frac{1}{2}N_C{}^c$, where $N_C{}^\circ$ is the number of moles of cyclopentadiene or $C_5$ residues in ester (I). This mode of computation is justified by experiments described on p. 1965, which showed that the polymerisation is practically complete. $N_E$ and $N_A$ were determined by electrometric titration of weighed quantities of solution, with an accuracy of $\pm 0{\cdot}2\%$; $N_A{}^\infty$ was determined 10 hr. after the start of the polymerisation. After the determination of $N_A{}^\infty$, an excess of 0·1N-alcoholic potassium hydroxide was added to the neutral reaction mixture; the alkaline solution was left for several hours at 25°, polymer (A) being completely hydrolysed. Back-titration showed that the number of moles of potassium hydroxide consumed, per kg. of solution, agreed to within $\pm 10\%$ with $N_A{}^\circ - N_A{}^\infty$ or with $N_E{}^\circ + N_A{}^\circ - N_A{}^\infty$. These results relate to polymers in the final reaction mixture; the *n*-values of precipitated polymers are somewhat higher, owing to greater solubility of homologues of low molecular weight.

Fig. 2 shows the results of a series of measurements in benzene at 25°; *n* values determined under different conditions are in Table 1. There appears not to be significant influence by initial concentration of cyclopentadiene, ester (I), trichloroacetic acid, or molecular oxygen. In all these experiments, *n* was measured at the end of reaction. Attempts were made to precipitate polymer (A) before reaction (2) had gone to completion, and to determine *n* of the precipitated material: the results were not reliable, possibly owing to occlusion or adsorption of unchanged ester (I)—the separation was made difficult by colloid chemical effects that will be described elsewhere. It could nevertheless be shown (see p. 1968) that *n* does not change between about 20% and 100% conversion.

TABLE 1. *Number-average degree of polymerisation, n, of polymer* (A) *prepared under different conditions.*

| Solvent | Temp. | Initial concn. (mole/l.) ester (I) | Initial concn. (mole/l.) $CCl_3{\cdot}CO_2H$ | *n* |
|---|---|---|---|---|
| $C_6H_6$ ........................... | 10° | 0·513 | 0·500 | 6·0 ± 0·6 |
| | 25 | 0·500—1·00 * | 0·0500—0·95 * | 7·0 ± 0·7 |
| | 35 | 0·513 | 0·0500 | 10 ± 1 |
| $CCl_4$ ............................... | 10 | 0·513 | 0·432 | 6·0 ± 0·6 |
| | 25 | 0·128—1·08 | 0·203—0·219 | 7·0 ± 0·7 |
| | 35 | 0·513 | 0·200 | 10 ± 1 |
| $C_6H_6$; 3·0M in $PhNO_2$ ...... | 25 | 0·505 | 0·200 | 12 ± 2 |
| $C_6H_6$; 0·3M in dioxan ...... | 25 | 0·300—0·900 | 0·200—0·400 | 7·0 ± 1·0 |

* Cf. Fig. 2. In one of these experiments the initial reaction mixture was made 0·024M with respect to polymer (A): there was no significant change in *n* of the final polymer.

*Rate of Trichloroacetic Acid-catalysed Polymerisation of Ester* (I).—This is represented by:

$$dy/dt = k(a - y)(b + y - y/n) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

where *a* and *b* are the initial concentration of ester (I) and trichloroacetic acid, *n* is the number-average degree of polymerisation, and *k* is the rate coefficient. Integration leads to

$$k = \frac{2{\cdot}30}{(b + \lambda' a)t}\left\{\log_{10}\left(\frac{a}{a - y}\right) + \log_{10}\left(\frac{b + \lambda' y}{b}\right)\right\} \quad . \; . \; . \; . \quad (7)$$

where $\lambda' = (n - 1)/n$ is assumed to be constant (cf. below). For the special case $b \gg a$ one obtains:

$$k = \frac{2{\cdot}30}{bt}\log_{10}\left(\frac{a}{a - y}\right) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

The concentration (*y*) of converted ester (I), was determined colorimetrically (the product being deeply coloured) or by titrating the liberated trichloroacetic acid; the latter method is, however, only applicable if $b$ is not much larger than $a$. In some experiments an aliquot part of the reaction mixture was $f$ times diluted (10—50-fold) with M-trichloroacetic acid in benzene, and the optical density, $\alpha$, of the diluted solution was measured in a cell of optical path length 0·0944 cm. at a wavelength close to one of the absorption peaks.[8] The time dependence of $\alpha$ was measured for the diluted solution and graphical back-extrapolation to the time of dilution was carried out. The first $\alpha$ values were measured about 2 min. after dilution. In other experiments atmospheric oxygen was excluded throughout, the optical density of the undiluted reaction mixture being determined after times $t$ and $t'$, thereby permitting computation of the velocity coefficient by Guggenheim's method.[11] In the experiments involving the titration by liberated ester, $y$ was calculated from:

$$y = [n/(n-1)]A_{\mathrm{t}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $n$ is the number-average degree of polymerisation and $A_{\mathrm{t}}$ is the acid concentration in excess of that added at zero time and corrected as indicated above. Results of such rate measurements in benzene, at 25°, are in Fig. 3, which shows that $k$ does not depend significantly on the initial concentration.* Rate coefficients were also determined under other conditions, a summary of all the measurements being in Table 2. The percentage of retardation was calculated as described for Table 3 of a preceding paper.[10] Other experiments showed that vigorous drying, traces of peroxides, and molecular oxygen do not influence the rate in benzene at 25°. When the first and the last three $k$ values of Table 2 are used the velocity coefficients in benzene and carbon tetrachloride can be represented, respectively, by:

TABLE 2. *Velocity coefficients, k, of conversion of ester* (I) *into polymer* (A). *Summary of results.*

| Temp. | Added substance (mole l.$^{-1}$) | $10^2k$ (l. mole$^{-1}$ min.$^{-1}$) | Added substance (mole l.$^{-1}$) | Retardation (%) | Temp. | $10^2k$ (l. mole$^{-1}$ min.$^{-1}$) |
|---|---|---|---|---|---|---|
| | *In* $C_6H_6$. | | *In* $C_6H_6$ *at* 25°. | | *In* $CCl_4$. | |
| 10° | — | 0·56 ± 0·08 | $H_2O$ (0·10) | 40 | 10° | 0·10 ± 0·02 |
| 25 | — | 1·5 ± 0·2 | $N^{IV}$ salt[b] (0·05) | 55 | 25 | 0·40 ± 0·05[c] |
| 35 | | 2·9 ± 0·4 | EtOH (1·0) | 80 | 35 | 1·2 ± 0·2 |
| 25 | Glass capillaries[a] | 1·4 ± 0·2 | $COMe_2$ (1·0) | 96 | | |
| 25 | $PhNO_2$ (3·0) | 2·4 ± 0·3 | Dioxan (0·30) | 95 | | |
| 25 | Polymer (A) (0·024) | 1·5 ± 0·2 | | | | |

[a] These increased the surface : volume ratio by a factor of 6. [b] Tri-isobutylammonium trichloroacetate. [c] Mean from a set of tests similar to those shown in Fig. 3.

$$k = 10^{4\cdot4\,\pm\,1\cdot0}\exp[(-11{,}000 \pm 1000)/\boldsymbol{RT}] \quad (\text{l. mole}^{-1}\ \text{sec.}^{-1})$$

and

$$k = 10^{8\cdot6\,\pm\,1\cdot5}\exp[(-17{,}000 \pm 2000)/\boldsymbol{RT}] \quad ,, \qquad ,,$$

In using expression (9) it was assumed that $n$ remains constant throughout the reaction, the final values being in fact employed. This is justified by the results shown in Fig. 4 and by the observed agreement of velocity coefficients calculated with the help of expression (9), with an $n$ value relating to 100% conversion and with the help of optical-density measurements.

*Rate of Formation of Polymer* (A) *if Cyclopentane is the Starting Material.*—The two simultaneous differential rate equations are:

$$\mathrm{d}x/\mathrm{d}t = k_1(c-2x)(b-x+y-y/n)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\mathrm{d}y/\mathrm{d}t = k(x-y)(b-x+y-y/n) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $c$ is the initial concentration of cyclopentadiene, $k_1$ is the velocity coefficient of reaction (1), its numerical value being one-half of the rate coefficient defined by equation 1 of a preceding paper,[10] $x$ is the concentration of ester (I) at time $t$, and the other symbols have the same significance as in rate equation (6). If the trichloroacetic acid concentration, $b$, is much larger

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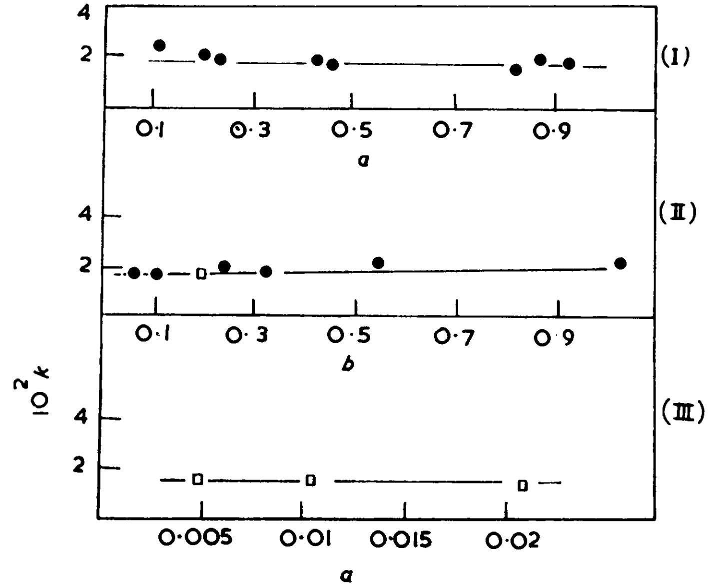
* For individual $k$ values in typical runs see ref. 6.

[11] Guggenheim, *Phil. Mag.*, 1926, **7**, 538.

than $c$, integration is possible, with the help of Laplace transform, but the velocity coefficients obtained in this way are not more accurate than those derived in a simple manner without integration. Differentiation of expression (11) and appropriate substitution lead to

$$k' = \frac{\ddot{y}/c + 2k_1'\dot{y}/c}{2k_1'(\frac{1}{2} - y/c) - \dot{y}/c} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

FIG. 3. *Rate of trichloroacetic acid-catalysed conversion of ester* (I) *into polymer* (A); *benzene at* 25°. *a*, *b*: *Initial concns. of ester* (I) *and trichloroacetic acid* (mole $l.^{-1}$) *respectively. Velocity coefficients, k, in* l. $mole^{-1}$ $min.^{-1}$.



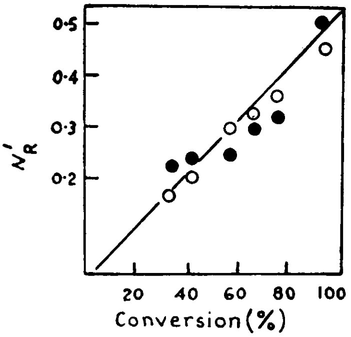
● *Titration of released trichloroacetic acid.* □ *Optical-density measurements.*

(I): $b = 0{\cdot}123 - 0{\cdot}403$; $10^2k$ (mean) $= 2{\cdot}0 \pm 0{\cdot}2$.
(II): $a = 0{\cdot}339 - 0{\cdot}448$; $10^2k$ (mean) $= 1{\cdot}8 \pm 0{\cdot}2$.
(III): $b = 0{\cdot}251 - 2{\cdot}09$; $10^2k$ (mean) $= 1{\cdot}6 \pm 0{\cdot}2$.

FIG. 4. *Trichloroacetic acid-catalysed conversion of ester* (I) *into polymer* (A); *benzene solution at* 25°. $N_R'$ = *number of* $C_{10}$ *residues per l. of solution incorporated into polymer. Initial concn.*: *ester* (I) 0·498M; *trichloroacetic acid* 0·500M.

○, *Calc. from expression* (9) *with the assumption that* $n = 7$, *throughout the run.*

●, *Calc. from results of electrical conductance measurements, with graphs similar to those shown in Fig.* 1.



where $k_1' = k_1b^2$ and $k' = kb$. The first and second derivatives, $\dot{y}/c$ and $\ddot{y}/c$, in (12) can be computed from a set of finite differences [12] (see Table 3), provided the experimental determination of $y/c$ is carried out at equal intervals ($\omega$) of time. For computation of the first derivative,

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[12] Milne, " Numerical Calculus," Princeton Univ. Press, 1949, Chapter VI; see also " Interpolation and Allied Tables," H.M. Stationery Office, London, 1936.

$\dot{y}/c$, a set of finite differences, $\Delta_0' = \frac{1}{2}(\delta'_{-\frac{1}{2}} + \delta'_{+\frac{1}{2}})$, $\Delta_1' = \frac{1}{2}(\delta'_{\frac{1}{2}} + \delta'_{\frac{3}{2}})$, etc., and $\Delta_0''' = \frac{1}{2}(\delta'''_{-\frac{1}{2}} + \delta'''_{+\frac{1}{2}})$, etc., is required. The first and second derivatives, for instance at time $t_0$, are given by:[12]

$$\left.\begin{aligned}\omega(\dot{y}/c)_{t=0} &= \Delta'_0 - \tfrac{1}{6}\Delta'''_0 + \tfrac{1}{30}\Delta_0^{\mathrm{V}}\ldots\ldots\\ \omega^2(\ddot{y}/c)_{t=0} &= \delta''_0 - \tfrac{1}{12}\delta_0^{\mathrm{IV}} + \tfrac{1}{90}\delta_0^{\mathrm{VI}}\ldots\ldots\end{aligned}\right\}\quad\ldots\ldots\quad(13)$$

and similarly for other $t$ values.

TABLE 3. *Finite differences of the type used for computation of the first and second derivatives in rate equation* (12).

| Time | Experimentally determined function of time | Finite differences | | | |
|---|---|---|---|---|---|
| | | $\delta'_{-3/2}$ | | | |
| $t_{-1}$ | $(y/c)_{t=-1}$ | | $\delta''_{-1}$ | | $\delta^{\mathrm{IV}}_{-1}$ |
| | | $\delta'_{-1/2}$ | | $\delta'''_{-1/2}$ | |
| $t_0$ | $(y/c)_{t=0}$ | | $\delta''_0$ | | $\delta_0^{\mathrm{IV}}$ |
| | | $\delta'_{+1/2}$ | | $\delta'''_{+1}$ | |
| $t_1$ | $(y/c)_{t=+1}$ | | $\delta''_{+1}$ | | $\delta^{\mathrm{IV}}_{+1}$ |

$(y/c)_t$ was determined experimentally by measuring in the absence of molecular oxygen, the optical densities including those corresponding to 100% polymerisation. For the present purpose it is sufficiently accurate to use only the first two terms on the right-hand side of expression (13), etc. The rate coefficients determined in this way are in the fifth column of Table 4. The values in the last column relate to experiments in which the isolated ester (I) was the starting material; the two sets of rate coefficients agree within the limits of the combined experimental errors.

TABLE 4. *Rate coefficients, k, of trichloroacetic acid-catalysed formation of polymer* (A). [*The k values relate to experiments in which the starting materials were respectively cyclopentadiene and the isolated ester* (I).]

| | | Initial concn. (mole l.$^{-1}$) | | $10^2k$ (l. mole$^{-1}$ min.$^{-1}$) | |
|---|---|---|---|---|---|
| Temp. | Solvent | $C_5H_6$ | $CCl_3{\cdot}CO_2H$ | from (12) | from (7) |
| 20° | $CCl_4$ | 0·0421 | 2·22 | 0·21 ± 0·03 | 0·28 ± 0·03 |
| 20 | ,, | 0·0413 | 1·12 | 0·20 ± 0·03 | |
| 20 | ,, | 0·00706 | 1·14 | 0·26 ± 0·04 | |
| 20 | $C_6H_6$ | 0·0220 | 2·09 | 1·0 ± 0·2 | 1·3 ± 0·2 |
| 20 | ,, | 0·0234 | 1·61 | 1·0 ± 0·3 | |
| 31 | ,, | 0·0240 | 0·544 | 1·4 ± 0·4 | 2·2 ± 0·4 |
| 40 | ,, | 0·0229 | 0·500 | 3·0 ± 0·6 | 4·0 ± 0·6 |

If $b$ and $c$ in expressions (10) and (11) are of the same order of magnitude, one rearranges and differentiates equation (11), thus obtaining:

$$x = \frac{b}{2} + \frac{(2n-1)}{2n}y - \sqrt{\left[\left(\frac{b}{2} - \frac{y}{2n}\right)^2 - \frac{1}{k}\dot{y}\right]}\quad\ldots\ldots\quad(14)$$

$$\dot{x} = \frac{(2n-1)}{2n}\dot{y} + \tfrac{1}{2}\left\{\frac{\left(\frac{b}{2} - \frac{y}{2n}\right)\frac{\dot{y}}{n} + \frac{1}{k}\ddot{y}}{\sqrt{\left[\left(\frac{b}{2} - \frac{y}{2n}\right)^2 - \frac{1}{k}\dot{y}\right]}}\right\}\quad\ldots\ldots\quad(15)$$

Introducing expressions (14) and (15) into (10) and determining $y$, $\dot{y}$, and $\ddot{y}$, as described above, leads to a biquadratic equation,[13] which can be solved for $k$. Some of the coefficients, however, are small differences of large quantities the accuracy of which is only 10—15% so that sufficiently accurate values of $k$ cannot thus be obtained. If, on the other hand, a velocity coefficient, $k$ from Table 2 or 4 is introduced into expression (14), the value of $x$ can be computed. Typical results are in Fig. 5, which also shows experimentally determined $y$ values. In the early stages

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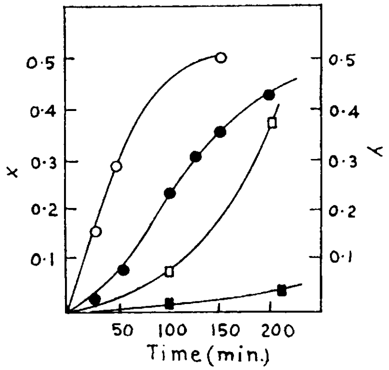
[13] See Appendix 4 of ref. 6.

of these reactions, $y$ is relatively small, which is to be expected, of course, in view of the preparative isolation[2] of ester (I).

*Oxidation of Ester* (I) *and of the Alcohol derived from It.*—Ozone was bubbled at −20°, for 13 hr., through a solution of ester (I) (25 g.) in ethyl acetate (100 ml.). After the solution had been left for 5 days at +20°, 30% hydrogen peroxide (25 ml.) in acetic acid (50 ml.) was added, and the whole was left at +20° for 12 hr. and refluxed for 30 min. The solvent and hydrogen peroxide were distilled off and the residue, a viscous paste, was dried. Sublimation at 160°/0·1 mm. gave succinic acid, m. p. and mixed m. p. 182° (from acetone), whose identity was confirmed by conversion into the *p*-bromophenacyl ester.

FIG. 5. *Trichloroacetic acid-catalysed conversion of cyclopentadiene into ester* (I) *and polymer* (A) *at* 25°; $x$ *and* $y$ (mole l.$^{-1}$) *are defined by rate equations* (10) *and* (11).



| Solvent | Initial concn. (M) $C_5H_6$ | $CCl_3{\cdot}CO_2H$ | Symbol |
|---|---|---|---|
| $C_6H_6$ ........................... | 0·972 | 1·00 | ○ ● |
| $CCl_4$ .............................. | 1·00 | 0·996 | □ ■ |

○ and □ relate to left ordinate: ● and ■ relate to right ordinate.

3-(Cyclopenta-2,4-dienyl)cyclopentanol[2] (4 g.) in benzene (500 ml.) and an aqueous solution (1100 ml.) of potassium permanganate (25 g.) and sodium carbonate (40 g.) were shaken for 2 days at 20° and then refluxed for 2 hr. After separation of the benzene layer, the pH of the alkaline solution was brought to 2·3 by addition of concentrated phosphoric acid, a precipitate being dissolved with 30% hydrogen peroxide. The resulting solution was extracted with boiling ether for 5 days; after drying and removal of ether, the residue was sublimed *in vacuo* and recrystallised from acetone, giving succinic acid, m. p. 182°, identified as above.

The mechanism of these oxidations is not known, but it can be concluded that the formation of succinic acid is preceded by a shift of hydrogen from positions 1′,3 to 2′,3′ (cf. ref. 14). This rearrangement is similar to one postulated below.

## DISCUSSION

*Kinetics.*—Conversion of ester (I) under catalysis by trichloroacetic acid into polymer (A) is kinetically similar to certain addition polymerisations[15] in which the growing polymer reacts with monomer, thereby forming products of relatively low molecular weight. The following reactions account for the observed kinetics:

Initiation: $C_{10}H_{13}B + HB \underset{k'}{\overset{k_i}{\rightleftharpoons}} (RB)^+ \cdots B^-$ . . . . . . . . . . (16)

Propagation: $(R_rB)^+ \cdots B^- + C_{10}H_{13}B \xrightarrow{k_p} (R_{r+1}B)^+ \cdots B^- + HB$ . . . . . . (17)

Termination: $(R_rB)^+ \cdots B^- + C_{10}H_{13}B \xrightarrow{k_{te}} (R_{r+1}B) + 2HB$ . . . . . . . . (18)

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[14] Formula (II) of ref. 2.

[15] Laible, *Chem. Rev.*, 1958, **58**, 807.

where $C_{10}H_{13}B$, HB, and R represent the ester (I), trichloroacetic acid, and $C_{10}$ residues incorporated into the growing carbonium ions, $R_rB^+$, and into the dead polymer homologues, $R_rB$, of degree of polymerisation $r$; $k_i$, $k'_i$, $k_p$, and $k_{te}$ are velocity coefficients. The termination (18) describes a situation in which the acid concentration is so low that the equilibrium [1] between dead polymer and acid is far on the side of the deprotonated species. If the acid concentration is high, *e.g.* M, the dead polymer is almost completely protonated.[1] The resulting dead carbonium-ion pairs [1] are assumed to be different from the growing carbonium-ion pairs formed in reactions (16) and (17), for reasons outlined on p. 1973. Both in the growing and in the dead carbonium-ion pairs the trichloroacetate counterion, $B^-$, must be firmly bound to the cation, because of the low dielectric constant of the solvent.

TABLE 5. *Numerical values of rate coefficients, $k_i$, ratios $k_{te}/k_p$ and of the relevant non-exponential A factors and activation energies, E.*

| Temp. | $10^3k_i$ (l. mole$^{-1}$ min.$^{-1}$) | $k_{te}/k_p$ | $\log_{10} A_i$ ($A_i$ in l. mole$^{-1}$ sec.$^{-1}$) | $E_i$ (kcal. mole$^{-1}$) | $\log_{10} (A_{te}/A_p)$ | $-(E_{te} + E_p)$ (kcal. mole$^{-1}$) |
|---|---|---|---|---|---|---|
| | | | *In* $C_6H_6$. | | | |
| 10° | 0·93 ± 0·09 | 0·25 ± 0·03 | 1·6 ± 1 | 8·3 ± 1 | −4 ± 2 | 4·5 ± 1·5 |
| 25 | 2·1 ± 0·2 | 0·20 ± 0·02 | | | | |
| 35 | 2·9 ± 0·3 | 0·13 ± 0·02 | | | | |
| | | | *In* $CCl_4$. | | | |
| 10 | 0·17 ± 0·02 | 0·25 ± 0·03 | 4·7 ± 1 | 13·3 ± 1 | | |
| 25 | 0·57 ± 0·06 | 0·20 ± 0·02 | | | | |
| 35 | 1·2 ± 0·1 | 0·13 ± 0·02 | | | | |

By assuming that the stationary-state approximation is valid, that $k_{te}/k_p = \lambda$ is independent * of $r$, and that $(k_p + k_{te})[C_{10}H_{13}B] \gg k'_i$, it can be shown that

$$-d[C_{10}H_{13}B]/dt = k_i\{(2\lambda + 1)/\lambda\}[C_{10}H_{13}B][HB] \quad . \quad . \quad . \quad . \quad (19)$$

$$n = (2\lambda + 1)/\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$f_m = \lambda(1 + \lambda)^2/(1 + \lambda)^{r+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$f_w = \{(132{\cdot}1r + 163{\cdot}4)/(1 + \lambda)^{r+1}\}\left\{132{\cdot}1\left[\frac{1}{\lambda^2} - \frac{1}{(1 + \lambda)^2}\right] - \frac{163{\cdot}4}{(1 + \lambda)^2\lambda}\right\} \quad (22)\dagger$$

where $-d[C_{10}H_{13}B]/dt$ and $n$ are the rate and the number-average degree of polymerisation, $f_m$ is the mole fraction and $f_w$ is the weight fraction of an $r$-mer. According to expressions (19) and (20) the rate of polymerisation is proportional to the first power of the ester and acid concentration and $n$ is independent of the initial concentrations and of the degree of conversion. All this is in agreement with the experimental results. The retardation by added proton-acceptors is qualitatively similar to effects observed in other reactions [9,10] involving proton-transfer.

If one attempted to explain only the kinetics of this polymerisation one could postulate an initiation $C_{10}H_{13}B + HB \longrightarrow C_{10}H_{13}^+ \cdots (BHB)^-$ and identity of $k_i$ with the velocity coefficient, designated in a previous paper [10] by $k_5'$. These suppositions,‡ however, do not account for the structural aspects to be discussed below. The principle of microscopic reversibility requires that on addition of trichloroacetic acid to ester (I) the intermediate [10] $i''$ is formed. It is possible, however, that $k_i > k_5'$, and in this case the formation of $i''$ would be kinetically without consequence.

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* The following formula can, however, also be derived if it is assumed that $\lambda$ depends on $r$ in the manner specified by Murphy and Wassermann.[16]

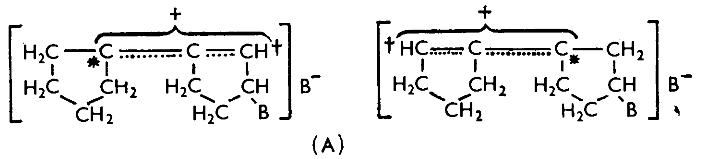
† Details of calculation are given in ref. 6, p. 82.

‡ It is recognised that such triple ions as $(BHB)^-$ are of importance for other reactions.[17]

[16] Murphy and Wassermann, *J. Polymer Sci.*, 1954, **14**, 477.

[17] Cf. Pocker, *J.*, 1958, 4327.

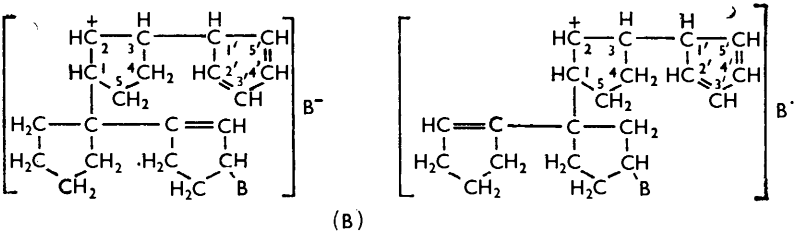
The numerical values of rate coefficient $k_i$ and ratios $k_{te}/k_p$ are in the second and third column of Table 5; they were calculated from the figures in the first three lines of columns 3 and 7 of Table 2, expressions (19) and (20) being taken into account. The relevant $A$ and $E$ values of the Arrhenius rate equation are also given in Table 5. The ratio $k_{te}/k_p$ (third column) decreases with increasing temperature, so that the activation energy of propagation, $E_p$, must be larger than the activation energy of termination, $E_{te}$; $k_p$ is nevertheless larger than $k_{te}$, the influence of the activation energies being over-compensated by that of the $A$ factors, as shown by the figures in the last two columns.



(A)

*Isomeric ion pairs formed in the initiating reaction* (16), *designated by* $(RB)^+ \cdots B^-$, R *being a* $C_{10}$ *residue. These species are formed if " end-on " protonation of the two conjugated carbon–carbon double bonds in ester* (I) *occurs. The isomer on the right is formed if hydrogen-shift occurs from positions* 3,1′ *to* 3′,4′; *the* 5′*-hydrogen atom is derived from the proton donor.*

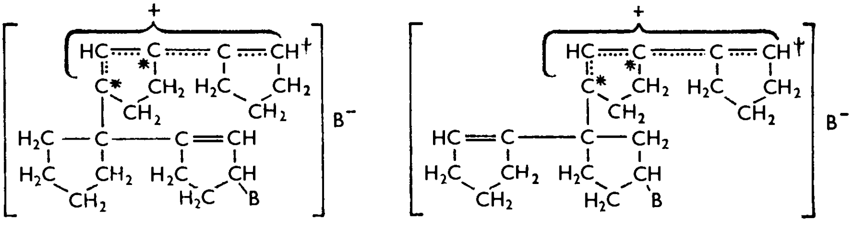
*The Build-up Principle.*—It is assumed that proton-transfer to ester (I) in the initiation reaction (16) is followed by a shift of hydrogen, thereby producing carbonium ions shown in (A). Oxygen of the trichloroacetate grouping in ester (I) may also be protonated, but this is not shown as it is not essential for this reaction. In the propagation steps (17), the elimination of trichloroacetic acid, HB, from ester (I), $C_{10}H_{13}B$, is regarded as a reverse acid addition to an olefin, $C_{10}H_{12}$, which participates in the formation of the growing carbonium ions, as shown in (B) and (C). This mode of reaction is assumed to be typical for all propagation steps. All growing carbonium ions are mesomers, so that each propagation step must lead to structural isomers, unless this interferes with stereochemical requirements; the number of structural isomers increases with increasing degree of polymerisation. In (A) and (C) some carbon atoms are indicated by asterisks or daggers, and these are, respectively the potential junction points of $C_{10}$ residues for propagation



(B)

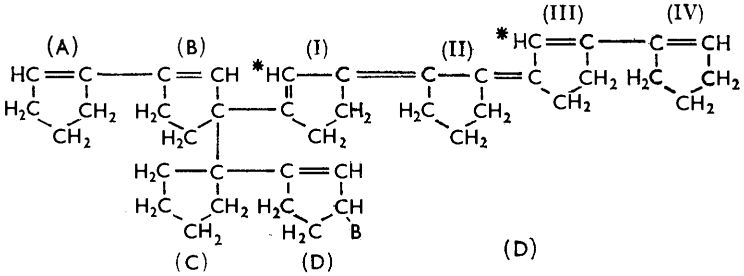
or termination. Carbon atoms indicated by an asterisk are joined to three others; those indicated by daggers are linked to two carbon and one hydrogen atom. In the termination step (18), elimination of trichloroacetic acid HB from ester (I), incorporation of the species $C_{10}H_{12}$, and rearrangement are assumed to occur, as they do in the propagation steps (17). The difference between the two steps (17) and (18) lies in the fact that species (C) and similar growing carbonium-ion pairs cannot be deprotonated with formation of a double bond between $C_{10}$ residues. In the carbonium ions formed in reaction (18), on the other hand, deprotonation with double-bond formation is possible, because the junction points between $C_{10}$ residues are carbon atoms of a different type, as indicated above and in the legends below (A). The structure of the carbonium ions formed in reaction (18) is such that deprotonation leads, not only to a new double bond, but also to a sequence of five conjugated double bonds if $r \geqslant 3$ and to a sequence of four conjugated double bonds if

$r = 2$. A typical deprotonated dead polymer homologue is shown in (D).* Proton-transfer to the five conjugated double bonds leads to the corresponding dead carbonium-ion pair, the mesomeric part of which is shown in Fig. 8b of the preceding paper.[1] Carbonium-ion pairs of this kind contain four formal conjugated double bonds, while the mesomeric part of the growing carbonium-ion pair (see C) contains only two formal conjugated double bonds. For this reason it is suggested that the dead carbonium-ion pairs are more stable. The polymer (D) contains also a sequence of two conjugated double bonds and one isolated double bond. Polymers in which $r > 4$ still contain only one sequence of five conjugated double bonds (formed in the termination), but the number of sequences of two conjugated double bonds or of isolated double bonds increases. If $r > 2$, straight-chain polymers in which successive $C_{10}$ residues are arranged in a linear fashion cannot be formed, non-linear species such as (D) being obtained.



(C)

*Growing carbonium ion pair, formed from the intermediate* (B) *by a shift of hydrogen from positions* 1,3, 1 *to* 2′,3′,4′. *These species are designated by* $(R_rB)^+ \cdots B^-$, *the degree of polymerisation, r, being* 2 *in this case.*



(D)

*Dead polymer homologue of degree of polymerisation,* $r = 4$. *In attempting to build up this species with space-filling models, there is no difficulty in joining together rings* A, B, C, D, *and* IV, *but some strain occurs in joining rings* I, II, *and* III. *Owing to the exocyclic double bonds two hydrogen atoms indicated* * *are forced close together; in order to accommodate them a coplanar orientation of rings* I, II, *and* III *has to be avoided.*

This build-up principle accounts for the observed[1] total number of double bonds; for the presence[1] of one trichloroacetate grouping,† B, in one mole of the polymer; for the non-linear structure;[1] for the presence of a long and a short sequence of conjugated double bonds, as indicated by the electronic spectrum[1] of the polymer; and for the kinetics of polymerisation.

The proton-transfer to ester (I) in reaction (16) or the elimination of trichloroacetic acid in reactions (17) and (18) may be synchronised with the shift of hydrogen indicated in the legend below (A) and (C) or with the formation of the bonds joining the $C_{10}$ residues, R, together, and with the subsequent rearrangements (see B and C). It is also possible, however, that reactions (16), (17), and (18) are each a set of consecutive processes, this not

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* The structure of similar species is shown in Figs. 20—22 of ref. 6.

† According to the suggested mechanism, the presence of the trichloroacetate grouping is due to the mode of initiation, not to the collapse of a growing carbonium-ion pair.

being incompatible with the assumption that the " over-all " initiation, propagation, and termination are each kinetically of the second order. The rearrangements, specified above, may be due to hydride-transfers, which have been invoked before to explain isomerisation occurring in cationic polymerisation [18] and carbonium ions occurring in other reactions.[19] This mechanism is more satisfactory than one involving a rapidly established pre-equilibrium between ester (I) and an isomer. It is admitted, however, that a pre-equilibrium could also be reconciled with the observed kinetics.

*Unsatisfactory Alternative Structure of Polymer* (A).—A different build-up principle could operate if all the double bonds in this polymer were conjugated. One could argue that this is actually the case and that the observed electronic spectrum of the polymer is to be regarded as superposition of the spectra of each polymer homologue. In order to find out whether this hypothesis is justified the over-all light absorption coefficients, $\varepsilon$, of the polymer were calculated with the help of appropriate mole fractions, $f_{\mathrm{m}}(r)$, taken from Fig. 6 and with $\varepsilon_r$ values taken from open-chain reference polyenes containing a known number of conjugated double bonds. The $\varepsilon$ values were represented by

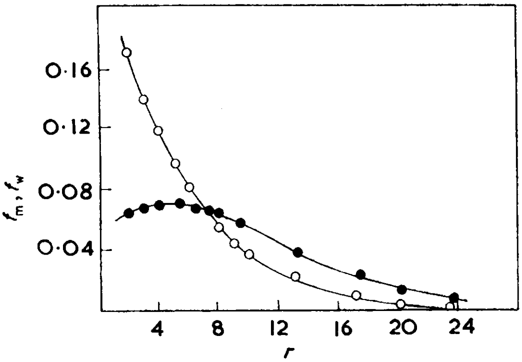

FIG. 6. *Molecular-weight distribution of polymer* (A) *in benzene at 25°, calculated from equations* (21) *and* (22).

○ *Mole fractions,* $f_{\mathrm{m}}$.
● *Weight fractions,* $f_{\mathrm{w}}$ (*not referred to in text*).

$$\varepsilon = \sum_{r=2}^{r=15} \varepsilon_r f_{\mathrm{m}}(r) + \sum_{r=16}^{r=\infty} \varepsilon_r f_{\mathrm{m}}(r) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (23)$$

where the $\varepsilon_r$ values in the first term on the right-hand side relate to reference polyenes [20] containing 2—15 conjugated double bonds, it being assumed that the values of the reference polyene and of the $r$-mers are identical if the number of conjugated double bonds is the same. Fig. 6 shows that the mole fractions $f_{\mathrm{m}}(r)$ become small if $r > 15$, and it is justified, as a first approximation, to calculate the last term of expression (23) on the assumption that the relevant light-absorption coefficients are the same as those of another open-chain reference polyene [22] with 19 conjugated double bonds (open-chain polyenes with more than 19 conjugated double bonds are not known). The superposition spectrum of polymer (A) calculated in this manner [23] shows peaks at 320, 440, and 480 mμ, with $\varepsilon$ values of about $3 \times 10^4$. In the observed electronic spectrum,[1] on the other hand, there are no peaks at wavelength longer than 360 mμ.

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE,
GOWER STREET, LONDON, W.C.1.

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[18] Fontana, " Cationic Polymerisation " (ed. Plesch), Heffer, Cambridge, 1953, p. 121.
[19] See, *e.g.*, Deno, Peterson, and Saines, *Chem. Rev.*, 1960, **60**, 7.
[20] Ref. 21 of the preceding paper.
[22] Karrer and Eugster, *Helv. Chim. Acta*, 1951, **34**, 1805.
[23] Cf. ref. 6, Appendix 8.