376. *Preparation and Properties of Deeply Coloured, Electrically Conducting Polymers.*

By P. V. French, L. Roubinek, and A. Wassermann.

Cyclopentadiene and four of its derivatives have been converted, under catalysis by trichloroacetic acid, into unsaturated polymers of molecular weight 1090—30,000, which are deeply coloured owing to the tail end of light-absorption peaks at 310—365 mμ and accept protons reversibly. The electronic spectra of the protonated polymers are characterised by peaks between 470 and 650 mμ. The equilibrium between these polymers and proton-donors has been studied and it has been shown, by measurements of electrical conductance, that the proton-transfer produces ion pairs; and the dissociation constants of these ion pairs have been determined. The electronic spectra and the proton-acceptor properties are explained by formation of a short and a longer sequence of conjugated double bonds.

It has been reported[1] that 3-(cyclopenta-2,4-dienyl)cyclopentanol and its trichloroacetate can be converted into deeply coloured polymers. It is now shown that cyclopentadiene, cyclopentenyl chloride, cyclopentadienylidenecyclopentane, and a colourless cyclopentadiene polymer can be converted into deeply coloured species, all these reactions being catalysed by trichloroacetic acid in aprotic solvents. We prove in what follows that these polymers are highly unsaturated, containing a longer and a shorter sequence of conjugated double bonds, and we establish the end group of one of the polymers; the stoicheiometry of polymerisation, and the structure of reactive entities or repeating units, are discussed in the following paper.[2]

Experimental

Cyclopentadiene was purified and dried as described by one of us elsewhere.[3] 3-(Cyclopenta-2,4-dienyl)cyclopentanol,[1] cyclopentenyl chloride,[4] and cyclopentadienylidenecyclopentane[5] were redistilled shortly before use, and were stabilised by 10^{-4} mole of α-tocopherol per l.

Most solvents and acids were dried and refractionated or recrystallised shortly before use. Dodecylbenzenesulphonic acid was a sample in which the position of the dodecyl group relative to the other substituent is not known.

Preparation of Polymers.—The temperature and concentration conditions of the trichloroacetic acid-catalysed polymerisations are indicated in Table 1. After the specified times the free acid was removed with potassium hydrogen carbonate, the colour of the solutions changing from deep blue to red-brown. The polymers were isolated by precipitation with 10 volumes of

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[1] Blakely, Gillespie, Roubinek, Wassermann, and White, *J.*, 1961, 1939.
[2] Murphy, Roubinek, and Wassermann, following paper.
[3] French, Ph.D. Thesis, London, 1958.
[4] Noeldechen, *Ber.*, 1900, **33**, 3348.
[5] Kohler and Kable, *J. Amer. Chem. Soc.*, 1935, **57**, 917.

ethanol, centrifugation, and drying *in vacuo*. Other precipitants for benzene, carbon tetrachloride, chloroform, carbon disulphide, or pyridine solutions are acetone, acetic acid, ether, and water. Some polymers were purified by repeated dissolution and precipitation or by chromatographic adsorption on calcium carbonate.

TABLE 1. *Preparation of deeply coloured polymers by trichloroacetic acid-catalysis in benzene,* 0·001M *with respect to α-tocopherol at* 25°.

Starting material (S.M.)	Initial concn. (mole/l.) S.M.	Initial concn. (mole/l.) $CCl_3{\cdot}CO_2H$	Reaction time (hr.)	Yield of polymer * (%)	Ref. design. of polymer
Cyclopentadiene	0·50—2·0	0·50—1·0	24	90	A
3-(Cyclopenta-2,4-dienyl)cyclopentanol	0·50	0·50	30—82	66	B
Cyclopentenyl chloride	1·0	0·50	16—113	27—28	C
Cyclopentadienylidenecyclopentane	0·50—1·0	0·50—1·0	18—22	63—75	D
Colourless cyclopentadiene polymer (E)	0·0017	1·0	25	70	F

* Calc. on starting material.

Comparing the oxygen and chlorine content of 3-(cyclopenta-2,4-dienyl)cyclopentanol and of cyclopentenyl chloride with the analyses of the relevant polymers (Table 2) indicates that respectively water and hydrochloric acid are released. This was directly proved by Karl Fischer titrations and by distilling the hydrochloric acid into traps containing standard alkali.

TABLE 2. *Analytical composition, molecular weights, bromine consumption, and viscosity number of polymers.*

Polymer	C (%)	H (%)	Cl (%)	O (%)	10^{-3}M	Br_2 (mol.)	$10^2[\eta]$ [e]
A	81·2 ± 0·2	7·91 ± 0·2	7·60 ± 0·3	3·3 ± 0·7	1·2 ± 0·2 [c]	15 ± 1	4·0 ± 0·3
A [a]	84·0 ± 0·3	8·60 ± 0·3	<0·3	9·4 ± 0·6 [b]	—	—	—
B	86·3 ± 0·3	8·43 ± 0·3	2·72 ± 0·3	2·5 ± 1·0	3·3 ± 0·1 [c]	36 ± 4	5·0 ± 0·3
C	83·9 ± 0·4	8·70 ± 0·3	6·70 ± 0·3	0·7 ± 1·0	1·09 ± 0·3 [c]	9 ± 1	3·5 ± 0·2
D	86·0 ± 0·3	8·70 ± 0·3	2·49 ± 0·4	2·8 ± 1·1	4·2 ± 0·1 [c]	45 ± 4	9·0 ± 0·4
E	83·8 ± 0·3	9·08 ± 0·3	6·42 ± 0·3	0·7 ± 0·9	32 ± 5 [d]	225 ± 30	10 ± 1
F	86·0 ± 0·3	8·68 ± 0·3	3·70 ± 0·3	1·6 ± 0·9	30 ± 5 [d]	290 ± 30	11 ± 1

[a] Polymer A′ is the hydrolysis product of the ester polymer A. [b] The relatively high oxygen content is due to oxidation during alkaline hydrolysis and purification; these operations were carried out without antioxidant. [c] Number average. [d] Weight average. [e] In C_6H_6 at 25° (100 ml. of soln. per g.).

Polymer (E), the colourless starting material of polymer (F) (for reference designations see Table 1), was prepared from commercial stannic chloride [5a] (0·15 mole $l.^{-1}$) and cyclopentadiene (3·0 moles $l.^{-1}$) in chloroform containing α-tocopherol (0·0095 mole $l.^{-1}$). The stannic chloride was added dropwise, in 5 min., to the solution which was stirred at −5°; after 15 min. the temperature had risen to +6°; pyridine (0·3 mole $l.^{-1}$) was added, precipitating the stannic chloride as an adduct. This adduct was removed by centrifugation and the liquid was added to 10 volumes of ethanol; polymer E was thus precipitated and it was dried *in vacuo*.

Methods of Investigation.—The infrared absorption of polymer A was measured with a Perkin–Elmer instrument, for films and solutions in carbon tetrachloride, chloroform, and carbon disulphide, exposure to air being as short as possible.

Bromination and hydrogenation of the polymers were carried out by methods similar to those described elsewhere.[1,6]

Polymer solutions free from peroxides and air were prepared in a vacuum-vessel, V, fitted with a glass or plastic membrane tap,[6] sugar grease [7] being used in the former case. The starting materials were passed through a column of activated alumina, and the effluent was

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[5a] Staudinger and Brusson, *Annalen*, 1926, **447**, 118.

[6] For details see Roubinek, Ph.D. Thesis, London, 1960.

[7] Meloche and Frederick, *J. Amer. Chem. Soc.*, 1932, **54**, 3264.

tested for peroxide;[8] if this was absent, the effluent, together with solvent, was placed in vessel, V, and, after removal of air at a pressure $<10^{-3}$ mm., dry, air-free trichloroacetic acid solution was added through a vacuum adaptor, W.[9] The acid solution had been prepared from a film of trichloroacetic acid, made *in vacuo*.[10]

For determination of the electronic spectra of polymers in absence of air, a vessel, V′, shown in Fig. 1 was used. After the side-arm had been filled by tilting, the vessel was introduced into a Unicam S.P. 500 spectrophotometer, without the vacuum's being released. Before the optical densities were measured, the solution in vessel V′ could be diluted with air-free acid solution which was transferred through an adaptor, W.

To remove free trichloroacetic acid in absence of air, the acid solution was transferred from vessel V, through adaptor W, into a second evacuated vessel, V″, containing dry, finely powdered potassium hydrogen carbonate, and the resulting potassium trichloroacetate was filtered off *in vacuo*.[10a] The filtrate was diluted with air-free solvent and transferred through adaptor W into vessel V′. The concentration of the final solution was estimated from the weights of starting material, acid, solvent and acid-free filtrate. If the cyclopentadiene concentration was too low to be accurately determined by weighing, it was calculated from the weight of solvent and the volume of air-free cyclopentadiene vapour of known temperature and pressure. In these experiments, vessel V′ had a restriction at the position shown in the Fig. 1, where it was then sealed off *in vacuo*. In all these tests the optical densities of the solutions without polymer were separately determined.

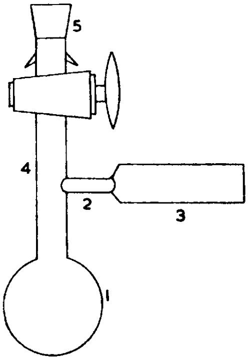

FIG. 1. *Apparatus.*

1, *Pyrex glass vessel*; 2, *graded seal*; 3, *silica light-absorption cell, path length* 0·102 *or* 0·700 *cm.*; 4, *position of restriction in glass tubing* (*see text*); 5, *connexion to vacuum-line.*

A few electrical-conductance measurements in absence of air and peroxides were also carried out: the solution in vessel V was transferred, through the adaptor W, into the evacuated conductance cell, which permitted determination of the resistance, by a technique described previously,[11] without release of the vacuum.

The number average molecular weights of polymers (A)—(D) were measured ebullioscopically by means of an apparatus similar to that described by Ray,[12] usually with *p*-xylene as solvent. The weight average molecular weights of polymers (E) and (F) were deduced from measurements of the refractive-index increment and from light-scattering tests in benzene ($2{\cdot}00 \times 10^{-4}$M in α-tocopherol) carried out with a Rayleigh interferometer and a Brice–Phœnix light-scattering instrument. The latter instrument was calibrated according to directions of Brice, Halwer, and Speiser,[13] the results being checked with Ludox solution [14] and with a polystyrene of known molecular weight. Solutions and solvent were freed from dust by filtration into semioctagonal cells of known dimensions,[15] through dust-free, sintered-glass filters (porosity no. 5) under slight pressure. Filters, light-scattering cells, and pipettes were cleaned with dust-free acetone and kept in special containers. The dissymmetry measurements were corrected as described by

[8] Kharasch, *J. Amer. Chem. Soc.*, 1933, **55**, 2468.
[9] Cf. Fig. 3 of ref. 3.
[10] Wassermann, *J.*, 1959, 989.
[10a] Blakely, Ph.D. thesis, London, 1957.
[11] Wassermann, *J.*, 1954, 4329.
[12] Ray, *Trans. Faraday Soc.*, 1952, **48**, 809.
[13] Brice, Halwer, and Speiser, *J. Opt. Soc. Amer.*, 1950, **40**, 768.
[14] Kraut and Dandliker, *J. Polymer Sci.*, 1955, **18**, 563.
[15] Frank and Ullman, *J. Opt. Soc. Amer.*, 1955, **45**, 471.

Sheffer and Hyde.[16] For polymer (E), the Cabannes correction factor was also measured and found to be insignificant; this was also so for three similar polymers.[3]

In determining the ratios, R_{90}, R_{45}, and R_{135} of polymer (F), the influence of its colour had to be taken into account, by measuring the optical density of each solution used for light scattering and by applying the corrections of Brice, Nutting, and Halwer [17] and of Frank and Ullman.[15] Scattering tests with polymer E were carried out with light of 546 mμ in the range 0·6—5·7 g. of polymer per 100 ml. of solution, while polymer F was investigated with light of 578 mμ in the range 0·06—0·28 g./100 ml.; five concentrations were tested in each case. The refractive index increments (at 25°) of polymers E and F were respectively 0·0372 ± 0·005 (546 mμ) and 0·104 ± 0·006 cm.^{3} g.$^{-1}$ (578 mμ).

The equilibrium coefficients, K, in Table 5 and the electrical conductances were measured with freshly prepared solutions, which had been exposed to air as shortly as possible. Back-extrapolation [11] of optical densities and electrical resistance to the time of mixing were carried out in all cases. Prolonged exposure of the solution to air reduced the K values. Determination of optical densities above or below room temperature is described elsewhere.[2]

RESULTS

Some Properties of Polymers.—At least three different batches of each polymer were prepared. The figures in columns 2—5 of Table 2 are means of analyses of each batch. The approximate temperature of decomposition was 200° for polymers (A), (A′), (B), (C), (D), and (E) and 100° for polymer (F). The colour of 0·1% benzene or chloroform solutions of these polymers is similar to that of aqueous 0·1N-iodine, but darkens when the solutions are shaken with acid or antimony trichloride.[6] Polymer (A) is amorphous, according to its *X*-ray powder diagram. This polymer showed strong infrared absorption peaks at 3021, 2920, 2890, 2860, 1773, 1695, 1577, 1366, 1260, 1251, 790, 741, 727, and 725 cm.$^{-1}$; medium and weak peaks were at 3640, 3620, 3570, 3436, 1464, 1073, 1000, and 910 cm.$^{-1}$. Heating polymer (A) at 350° in a stream of pure nitrogen caused evolution of carbon dioxide and hydrochloric acid, the dark brown solid residue being insoluble in benzene.

Polymer (A) is an ester of trichloroacetic acid, one mole of polymer containing one mole of trichloroacetate. This is proved by alkaline hydrolysis and is in accordance with the chlorine content. In isolating the alcoholic component (A′) of this polymer,[6] it was found that the only chlorine-containing product was potassium trichloroacetate, identified by conversion into its *S*-benzylthiouronium salt. The presence of the trichloroacetate groups in polymers (B) and (D) is made probable by their chlorine content and by the results of semiquantitative alkaline hydrolysis. The bromine consumption of polymer (A) (Table 2) agrees, within the limits of experimental error, with the results of catalytic hydrogenation.

The high degree of unsaturation of this polymer is confirmed by the following observations: 1 g. of polymer (A) was exposed for 9 months to dry air at 20°, the product (a) being extracted with hot dioxan; 0·034 mole of perbenzoic acid and 1 g. of polymer (A) in 190 ml. of benzene were left for 2 weeks at 7°, precipitation with light petroleum (b. p. 60—80°) then giving the product (b); ozone was bubbled for 20 hr. at 20° through a solution of 3 g. of polymer (A) in 100 ml. of carbon tetrachloride, thereby producing a precipitate (c). These faintly yellow or white products were centrifuged off, dried, and analysed, the yields being about 80% of the weight of the starting materials. Analysis indicated that the approximate average composition of the materials (a) and (b) is $(C_5H_6O)_x$ and that of material (c) is $(C_5H_6O_3)_x$. Degradation of the stable ozonide (c) with hydrogen peroxide was attempted, but crystalline materials could not be isolated.

Polymer (A) and maleic anhydride react with each other in benzene at 20°, to form a " copolymer " of number average molecular weight 4300 ± 500, not a simple Diels–Alder adduct.[6]

Electronic Spectra.—These polymers are characterised by a light-absorption peak at 250—252 mμ and by a peak or shoulder between 310 and 365 mμ (Table 3). Here and below, molar light-absorption coefficients, ε, were calculated on the basis of the molecular weights given in Table 2. The colour of the polymers is due to the tail of one of the peaks or shoulders; $\lambda_{\frac{1}{2}}$ in Table 3 is the wavelength at which ε is one-half of the value listed in the sixth column. The

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[16] Sheffer and Hyde, *Canad. J. Chem.*, 1952, **30**, 817.

[17] Brice, Nutting, and Halwer, *J. Amer. Chem. Soc.*, 1953, **75**, 824.

peaks in the spectrum of polymers (A), (B), and (D) could only be observed if peroxide and air were carefully excluded during preparation and measurement. Spectra of polymer (A) before and after exposure to air are shown in Figs. 2 and 3, similar effects being typical of all these polymers. The light-absorption peaks of polymers (C) and (F) could be detected in the presence of air for freshly prepared, relatively concentrated solutions, stabilised by α-tocopherol.

TABLE 3. *Electronic spectra of deeply coloured polymers at 20°.*

(sh = " shoulder "; the significance of $\lambda_{\frac{1}{2}}$ is explained in the text.)

		$\lambda_{\text{max.}}$ (mμ)		$10^{-3}\varepsilon$		$\lambda_{\frac{1}{2}}$
Polymer	Solvent [a]	(I)	(II)	(I)	(II)	(mμ)
A	Cyclohexane [b]	252	360	12 ± 1	5 ± 1	425
B	Cyclohexane [b]	251	310—320sh	106 ± 10	33 ± 3	355
C	Dioxan [c]	252	350	15 ± 1	10 ± 1	425
D	Cyclohexane [d]	250	~350sh	100 ± 10	26 ± 3	400
F	Cyclohexane [c]	254	365	78 ± 15	60 ± 15	480

[a] The polymerisation was carried out in carbon tetrachloride, an aliquot part being diluted with the solvents specified below, after completion of the reaction. Under the conditions of the optical-density measurements, the carbon tetrachloride concentration was sufficiently low to permit the detection of peak (I). [b] Air and peroxides excluded. [c] Air excluded. [d] Air present; solutions stabilised by α-tocopherol (0·002—0·005M); exposure to air as short as possible.

TABLE 4. *Electronic spectra of deeply coloured polymers in* M-*trichloroacetic acid at 20°.*

		λ (mμ)			$10^{-3}\varepsilon$		
Polymer	Solvent	(I)	(II)	(III)	(I)	(II)	(III)
A	C_6H_6 [b]	480(sh)	520	610	6·0 ± 1·0	7·4 ± 1·0	5·6 ± 1·0
	CCl_4 [b]	470	520(sh)	610	4·6 ± 1·0	3·3 ± 0·8	4·5 ± 1·0
B	C_6H_6 [c]	470(sh)	570(sh)	610	19 ± 1·0	30 ± 3	31 ± 1
	C_6H_6 [d]	480	580	—	14 ± 1	16 ± 1	—
	CCl_4 [c]	480	580	—	18 ± 2	25 ± 2	—
C	C_6H_6 [d]	480	510	625	7·0 ± 0·6	6·5 ± 0·6	7·4 ± 0·6
D	C_6H_6 [d]	480	580	—	21 ± 3	22 ± 3	—
	CCl_4 [c]	480	580(sh)	630	31 ± 4	15 ± 4	20 ± 3
F	Cyclohexane [d]	480	—	650	36 ± 10	—	60 ± 20
	C_6H_6 [d]	480	—	650	33 ± 10	—	50 ± 15
	CCl_4 [c]	475	603	653	21 ± 7	80 ± 25	70 ± 20

[b, c, d] See Table 3.

On addition of trichloroacetic acid, the polymers are converted into species the spectra of which are markedly altered, as shown in Fig. 3 and by the position of the peaks and shoulders in Table 4. The shape of these spectra depends on the acid concentration, up to ~1M, after which no further significant change occurs. This change is due to proton transfer from the acid to the polymer. The transfer is reversible, for if the free trichloroacetic acid is removed with potassium hydrogen carbonate in absence of air, the spectrum before addition of acid is restored. [If a benzene solution, 1·0M in trichloroacetic acid and 0·0010M in polymer (A), is exposed to air for 60 min. (rather than for the longer time mentioned in the legend of Fig. 3), the peaks of the spectrum are not destroyed, but one of them is shifted to 625 mμ, while the shoulder migrates to 560—570 mμ.] Beer-Lambert's law is obeyed in all these experiments. Polymer (A) was fractionally precipitated, thereby affording samples of number average molecular weights 947, 1012, 1083, 1088, 1300, and 1635, exposure to air being as short as possible. The spectra of these fractions in benzene, 1·0M with respect to trichloroacetic acid, were all similar to graph (b) in Fig. 3, there being no detectable trend of $\lambda_{\text{max.}}$ or $\varepsilon_{\text{max.}}$. Tests between 1000 and 2000 mμ with and without trichloroacetic acid were carried out, but no new peak due to electronic transitions was observed. The spectra of M-trichloroacetic acid solutions are characterised by tails stretching, in some cases, into the infrared range, as shown in Fig. 3; $\lambda_{\frac{1}{2}}$, the wavelength at which ε is one-half of the values listed in the last column of Table 4, is between 650 and 820 mμ. Attempts were made to find out whether the peak at 250—252 mμ (Table 3) occurs also with M-trichloroacetic acid solutions, but the results were inconclusive because the presence of acid prevented sufficiently accurate tests in this region.

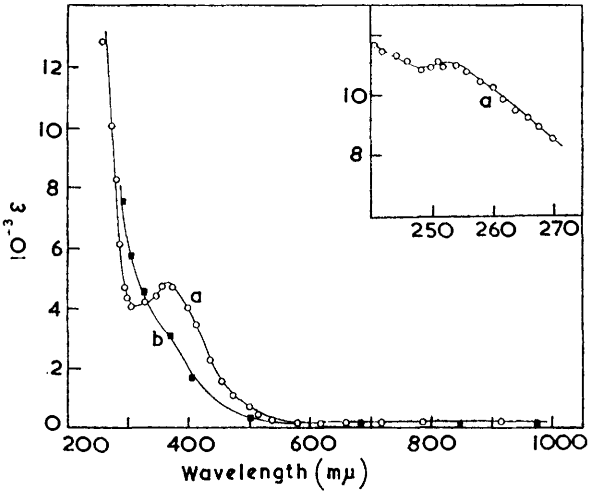


FIG. 2. *Electronic spectrum of polymer* (A), *at* 20°. *Solvents*: CCl_4 *for* 1000—480 mμ; *cyclohexane*-CCl_4 (0·729—0·360M *in* CCl_4) *for* 480—280 mμ.

Molarity of (A): 1·24 × 10^{-2}—7·45 × 10^{-4}; *optical path length* 0·102 cm.

(a) *Oxygen and peroxides rigorously excluded.* (b) *The same solution exposed during* 70 hr. *to air of atmospheric pressure at* 20°.

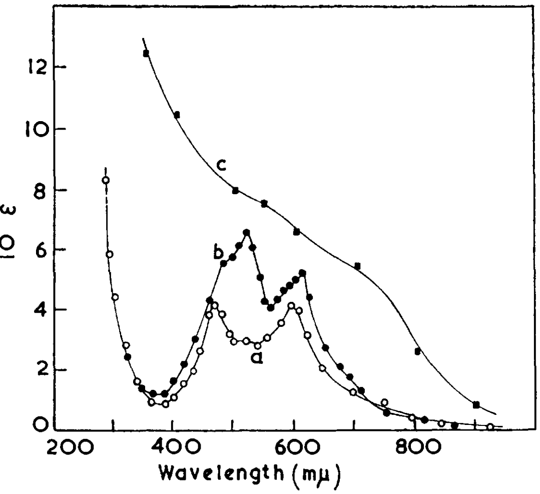


FIG. 3. *Electronic spectrum of polymer* (A) *in* 1·12M-*trichloroacetic acid at* 20°; *optical path length* 0·102 *cm.*

(a) *Solvent*: CCl_4; *molarity of polymer* (A) = 1·95 × 10^{-3} (O_2 *excluded*). (b) *Solvent*: C_6H_6; *molarity of polymer* (A) = 1·10 × 10^{-3} (O_2 *excluded*). (c) *Solvent*: CCl_4; *molarity of polymer* (A) *as in* (a); *the solution was originally free from molecular oxygen and peroxides, but had been exposed for* 240 *hr. to air of atmospheric pressure at* 20°.

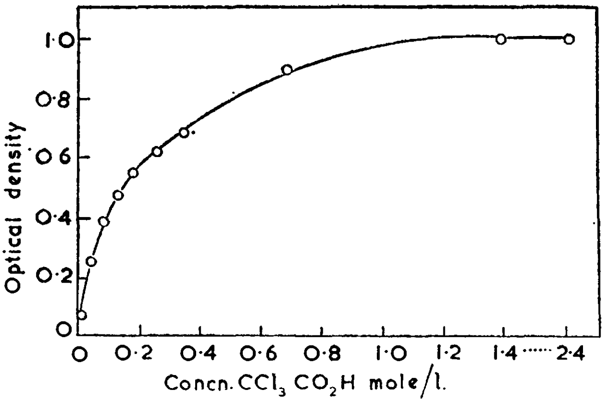


FIG. 4. *Optical density of polymer* (A) *in benzene at* 20°, *as a function of the trichloroacetic acid concentration. Polymer concn.* = 4·14 × 10^{-4} mole-l.; *optical path length* 0·516 cm.; 600 mμ; *optical densities extrapolated to the time of mixing.*

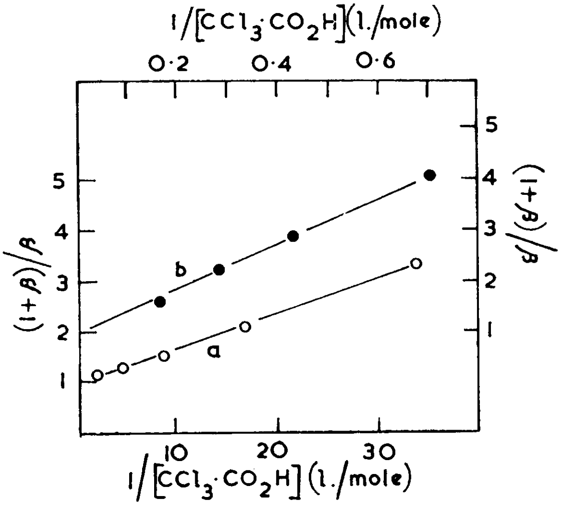
There is no peak between 470 and 260 mμ, the ε values increasing continually at wavelengths below 380 mμ.

The spectra of oxygen- and peroxide-free benzene solutions of polymer (A) (5×10^{-4}M) containing hydrochloric acid (0·3M), dodecylbenzenesulphonic acid (0·3M), or dichloroacetic acid (1·6M) are similar to those shown in Fig. 3a.

Proton-transfer Equilibria.—The reversible shift of the electronic spectra, in an aprotic solvent, on addition of trichloroacetic acid, is due to a proton transfer that produces ion pairs in which the acid anion is firmly bound to the protonated polymer cation. If [P] is the concentration of the polymer not combined with acid, the ratio [Ion pair]/[P] = β can be deduced from

FIG. 5. *Relation between* $(1 + \beta)/\beta$ *and the reciprocal of the acid concentration; benzene;* 20°. *For definition of* β *see text.*

(a) *Polymer* (F) *and trichloroacetic acid; left ordinate, lower abscissæ; polymer concn.* $0{\cdot}124 \times 10^{-4}$ *and* $1{\cdot}24 \times 10^{-4}$M; $\lambda = 650$ mμ. (b) *Polymer* (A) *and dichloroacetic acid; right ordinate, upper abscissæ; polymer concn.* $2{\cdot}07 \times 10^{-4}$ *and* $4{\cdot}14 \times 10^{-4}$M; $\lambda = 470$ *and* 560 mμ.



$$\beta = (d_A - d_0)/(d_\infty - d_A)$$

where d_A is the optical density of the polymer solution, containing acid of concentration [HA], d_0 is the optical density of the same solution without acid, and d_∞ is the optical density if [HA] is so high that practically complete protonation of the polymer occurs. Fig. 4 shows the results of typical experiments in which the optical density of a polymer solution as function of [HA] was determined, d_∞ being reached if [HA] is $> 1{\cdot}4$M. A knowledge of β enables one to compute the ratio:

$$[\text{Total polymer}]/[\text{Ion pair}] = (1 + \beta)/\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This is important because a plot of $(1 + \beta)/\beta$ against 1/[HA] is linear, in all the systems here considered, as shown for typical cases in Fig. 5. Such graphs can be extrapolated to 1/[HA] = 0, thereby obtaining the maximum number, *m*, of moles of acid bound by one mole of polymer. The intercepts of the graphs in Fig. 5 and the results of similar experiments show that *m* is $1{\cdot}0 \pm 0{\cdot}1$, and, therefore, the equilibrium coefficient, *K*, of the reversible reaction:

$$\text{Polymer} + \text{Acid} \rightleftharpoons \text{Ion pair} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is represented by:

$$K = \frac{[\text{Ion pair}]}{[\text{Polymer}][\text{HA}]} \cdot \frac{f(\text{ion pair})}{f(\text{polymer}) \cdot f(\text{HA})} = \frac{\beta}{[\text{HA}]} \cdot f \quad . \quad . \quad . \quad . \quad (4)$$

where *f* is the ratio of the three activity coefficients specified by the parentheses. It was found that in all cases log β is a linear function of log [HA], the slope of the graph being unity, within the limits of experimental error. (Similar observations were made with all other acids and polymers.) Thus *f* must be independent of [HA], within the concentration range of these experiments, and it is assumed, as a first approximation, that *f* is unity and that the equilibrium coefficient, K, can be computed from the intercept of the log β–log [HA] graphs. Most of the K values in Table 5 were determined in this manner, except those in lines 7 and 8, which were calculated by Page's method,[18] without a knowledge of d_∞. The equilibrium coefficient in line 5 was calculated on the assumption that the d_∞ values of mono- and di-chloroacetic acid are equal; an experimental determination of the former value is not possible, because of the limited solubility of monochloroacetic acid and its relatively low acidity. Plotting the logarithm of the K values in lines 2, 4, and 5 of Table 5 against the logarithm of the dissociation constants, expressed in mole/l., of the three chloroacetic acids in water gave a linear functional relationship of the Brönsted type with the parameters 0·50 ± 0·2 and 1·5 ± 0·3.

TABLE 5. *Equilibrium coefficient, K, of proton-transfer to deeply coloured polymers, in benzene (except as specified).*

Polymer	Acid	Temp.	Concn. range Acid (mole/l.)	Concn. range Polymer (g./l.)	K (l./mole)
A	$CCl_3{\cdot}CO_2H$	15°	0·105—2·10	0·370	4·3 ± 0·5
A	,,	25	0·0435—2·44	0·0620—0·748	6·1 ± 0·5
A	,,	37	0·104—1·74	0·374	6·5 ± 0·5
A	$CHCl_2{\cdot}CO_2H$	25	0·155—3·48	0·0748—0·848	0·65 ± 0·1
A	$CH_2Cl{\cdot}CO_2H$	25	0·325—1·56	0·490—1·99	0·061 ± 0·02
A	HCl	20	0·00414—0·0414	0·134	25 ± 4
A	$C_6H_4R{\cdot}SO_3H$ [a]	20	0·0212—0·170	0·134	17 ± 4
A	Picric	20	0·0440—0·146	0·134	10 ± 3
A	$CCl_3{\cdot}CO_2H$	20	0·202—2·00	0·0239—0·239	3·0 ± 0·5 [b]
A′	,,	20	0·0440—2·44	0·0500	8 ± 2
B	,,	20	0·0313—1·74	0·115—1·15	6·3 ± 1
C	,,	20	0·0150—2·00	0·206 ± 2·06	11 ± 2
D	,,	20	0·0600—2·89	0·228—2·28	4·0 ± 1
F	,,	20	0·0300—1·50	0·572—5·72	14 ± 2

[a] Dodecylbenzenesulphonic acid. [b] In $CHCl_3$.

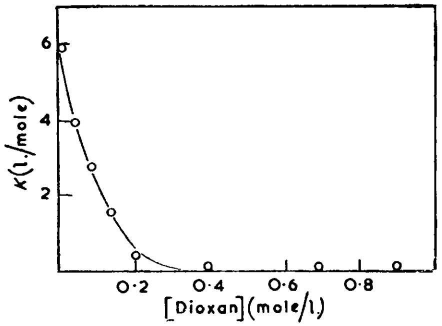


FIG. 6. *Influence of the basic solvent dioxan on the equilibrium coefficient, K, relating to polymer* (A) *and trichloroacetic acid; benzene solution;* 20°. *Concentration of polymer and acid respectively* 3·88 × 10^{-4}M *and* 0·140—1·95M.

If a benzene solution, 4·0 × 10^{-4}M in polymer (A) and 0·140M in trichloroacetic acid, is made 0·040M with respect to piperidinium trichloroacetate, or 2·0M with respect to ethanol or acetone, the equilibrium coefficient, K, decreases to respectively 2·0 and $<0{\cdot}1$ l. mole^{-1}. Fig. 6 shows similar effects with dioxan. In all these experiments β was calculated on the assumption that d_∞ is not altered by added substances.

Electrical Conductance.—The specific electrical conductance, κ, of a benzene solution 1·00M in trichloroacetic acid or 0·0500M in polymer (A) at 25° is respectively $<10^{-10}$ or $<10^{12}$ Ω^{-1} cm.$^{-1}$; if, however, the solution contains both the acid and the polymer, κ is 2·40 × 10^{-7} Ω^{-1} cm.$^{-1}$. Similar effects, observed with five other proton donors and with polymers B—F, are due to ion pairs formed in reaction (3). The ion-pair concentration, c', can be calculated, if one knows the equilibrium constant, K, of equation (4) and the stoicheiometric polymer concentration. The molar conductance, Λ, of the ion pairs is defined by:

$$\Lambda = (\kappa_{ev} - \kappa_{acid})/c' \qquad (5)$$

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[18] Page, *Trans. Faraday Soc.*, 1953, **49**, 637.

where κ_{ov} and κ_{acid} are respectively the over-all specific conductance of the solution and the specific conductance of the solution containing acid without polymer. In most tests κ_{acid} was less than 0·15 κ_{ov}. The ion pairs, $^{+}\text{PH} \cdots \text{Anion}^{-}$, dissociate, at sufficiently low concentration, according to:

$$^{+}\text{PH} \cdots \text{Anion}^{-} \overset{K_d}{\rightleftharpoons} \text{PH}^{+} + \text{Anion}^{-} \qquad (6)$$

the polymer cation, PH^{+}, and the acid anion being regarded as carriers of the electrical current; K_d, the dissociation constant of the binary ion pairs, is defined by:

$$K_d = \frac{[\text{PH}^{+}][\text{Anion}^{-}]}{[\text{PH}^{+} \cdots \text{Anion}^{-}]} \cdot \frac{f(\text{PH}^{+}) \,.\, f(\text{Anion}^{-})}{f(\text{PH}^{+} \cdots \text{Anion}^{-})} \qquad (7)$$

where the f's are activity coefficients. If we assume, as a first approximation, that the ratio of the f's is unity and that the dissociation of the acid in benzene is not significant,[10] it follows from equation (7) that:

$$\log \Lambda = -\log c' + \tfrac{1}{2}(\log K_d + 2 \log \Lambda_0) \qquad (8)$$

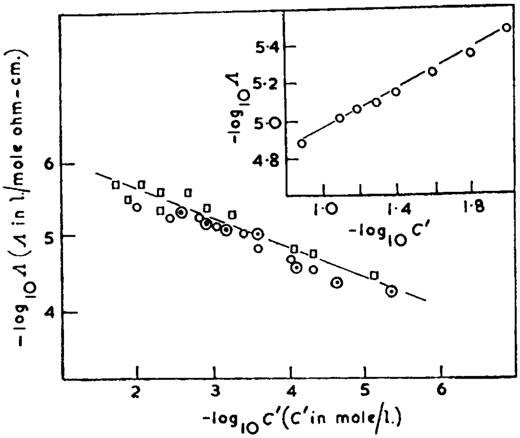


FIG. 7. *Relation between logarithm of molar electrical conductance* (Λ *in l. mole*$^{-1}$ *ohm*$^{-1}$ *cm.*$^{-1}$) *and logarithm of ion-pair concentrations,* c' (*mole l.*$^{-1}$). *The ion-pairs are formed by proton-transfer to polymer* (A); *benzene*; 25·0°. ○, □, *and* ⊙ *relate to tri-, di-, and mono-chloroacetic acid respectively as proton-donors.*

TABLE 6. *Results of electrical conductance measurements in benzene at* 25·0°.

K_d is the dissociation constant of binary ion pairs formed by proton-transfer to deeply coloured polymers. c' = concn. of ion pairs in mole/l. Λ in mole^{-1} Ω^{-1} cm.$^{-1}$ l.

Polymer	Acid	Concn. of acid (mole/l.)	Range of $-\log_{10} c'$	No. of c' values tested	$-\log_{10}\Lambda$ for $c' = 10^{-3}$ mole/l.	$-\log_{10}\Lambda_0$	$-\log_{10} K_d$ (K_d in (mole/l.)
A	$CCl_3{\cdot}CO_2H$	1·00	2·0—4·3	15	5·20 ± 0·10	3·0 ± 0·5	6·8 ± 1·0
	$CHCl_2{\cdot}CO_2H$	1·00	1·7—5·1	13	5·20 ± 0·10	3·0 ± 0·5	7·2 ± 1·5
	$CH_2Cl{\cdot}CO_2H$	0·946	2·6—5·4	7	5·20 ± 0·10	3·0 ± 0·5	6·8 ± 1·5
	Picric	0·127	1·7—3·5	4	6·75 ± 0·10	5·0 ± 1·0	6·6 ± 2·5
	$C_6H_4R{\cdot}SO_3H$ [a]	0·256	2·1—3·5	3	4·80 ± 0·10	3·5 ± 0·5	5·4 ± 2·0
B	$CCl_3{\cdot}CO_2H$	1·00	2·9—6·4	9	4·50 ± 0·10	2·9 ± 0·2	5·8 ± 1·0
C	,,	1·00	1·8—4·8	4	5·20 ± 0·10	3·5 ± 0·5	5·8 ± 1·8
D	,,	1·00	2·6—7·9	8	4·90 ± 0·10	2·0 ± 0·5	8·6 ± 1·5
F	,,	1·00	3·6—4·6	4	4·70 ± 0·10	3·0 ± 0·5	6·4 ± 1·0

[a] Dodecylbenzenesulphonic acid.

where Λ_0 is the molar conductance extrapolated to $c' = 0$. In all experiments with these polymers a linear relation between log Λ and log c' with slope 0·50 ± 0·05 is observed, provided the ion-pair concentration is in the range given in the fourth column of Table 6. Typical graphs of this kind are on the left-hand side of Fig. 7. The ion-pair dissociation constant, K_d, can be determined by extrapolation to $-\log c' = 0$, thereby obtaining the intercept $i = \tfrac{1}{2}(\log K_d + 2 \log \Lambda_0)$, the limiting molar conductance being derived by the method used previously.[10] The results of the electrical conductance measurements are in Table 6. On the whole, the K_d

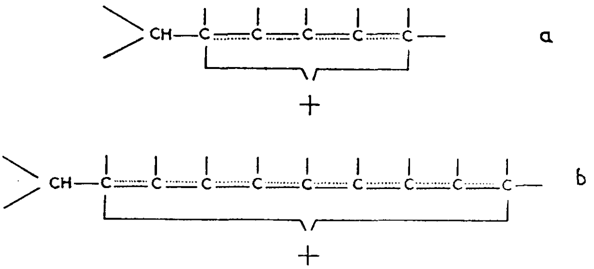
values are larger than those of binary ion pairs formed by proton-transfer to authentic conjugated polyenes.[10] In order to see, in one case, whether Λ_0 is correct and whether the assumption regarding the activity coefficient ratio in equation (7) is justified, K_d was calculated for the ion-pair formed from polymer (A) and trichloroacetic acid, with the help of a convergent extrapolation method.[10,19] The value so obtained agreed with that in the first line of the last column of Table 6.

The graph on the right-hand side of Fig. 7 shows that the molar conductance of the ion-pairs formed from trichloroacetic acid and polymer (A) increases with increasing concentration, if c' is larger than about 0·01M. The conductance minimum must be due to the influence of triple ions which are formed in the specified concentration range.[20] Tests with other polymers or acids in a similar concentration range have not been carried out.

DISCUSSION

Polymer (A).—Bromination, hydrogenation, and oxidation (p. 1956 and Table 2) show that there are 15 ± 1 double bonds per mole of polymer. Some of these double bonds must be conjugated, the two peaks of the electronic spectrum (see Fig. 2) being assigned to a sequence of respectively 2—3 and 4—6 conjugated double bonds. The numbers are estimated by comparison with electronic spectra of reference polyenes.[21] The experiments described in this paper do not enable one to decide whether this polymer contains also isolated double bonds, but other considerations [2] seem to indicate that both conjugated and isolated double bonds are formed.

FIG. 8. *Chromophores formed by " end-on " proton-transfer to a sequence of three or five conjugated double bonds in polymer* (A).



The presence of conjugated double bonds is confirmed by the observed proton-acceptor properties. As in the case of authentic conjugated polyenes,[10,11,22] a Brönsted-type relation has been observed (p. 1960), the dissociation constants, K_d, of binary ion pairs formed by protonation are much larger than the K_d values of substituted ammonium salts in the same solvent,[23] and the electronic spectra of the protonated species are shifted to longer wavelength. It has been shown that only one mole of proton-donor reacts with one mole of polymer and it follows that either the short or the long sequence of conjugated double bonds is protonated. If the shorter sequence consists of three double bonds, and if the proton is transferred to the end of the conjugated system, as in authentic conjugated polyenes,[24] a chromophore shown in Fig. 8a would be produced. In attempting to find out whether this can give rise to an electronic spectrum with peaks between 470 and 610

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[19] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476.

[20] For triple-ion formation in solvents of low dielectric constant see Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 2387, 3614; Hughes, Ingold, Patai, and Pocker, *J.*, 1957, 1206.

[21] Barrany, Braude, and Pianka, *J.*, 1949, 1898; Euler, Karrer, Klussmann, and Morf, *Helv. Chim. Acta*, 1932, **15**, 502; Karrer and Benz, *ibid.*, 1948, **31**, 1907; Kuhn, *Z. angew. Chem.*, 1937, **50**, 705; Karrer and Jucker, " Carotinoide," Birkhäuser, Basle, 1948, pp. 140, 200, 365; Smakula, *Z. angew. Chem.*, 1934, **47**, 664; Karrer, Eugster, and Faust, *Helv. Chim. Acta*, 1951, **34**, 823; Karrer and Leumann, *ibid.*, p. 445.

[22] Wassermann, *J.*, 1959, 983.

[23] Cf. Roubinek, Ph.D. Thesis, London, 1960, Appendix 5.

[24] Wassermann, (*a*) *J.*, 1959, 979; (*b*) *J.*, 1960, 891; *Mol. Phys.*, 1959, **2**, 226.

mμ (see Fig. 3 and Table 4) a simple free-electron treatment[25] of the spectra of mesomeric ions is used from which it follows that:

$$1/\lambda_1 = (V_0 - \boldsymbol{hc})(1 - 1/\boldsymbol{N}) + (\boldsymbol{h}/8\boldsymbol{mc})(\boldsymbol{N} + 1)/L^2 \quad . \quad . \quad . \quad (9)$$

where λ_1 is the wavelength of the peak, V_0 is the amplitude of a one-dimensional potential operating on the π-electrons, L is the chromophore length, computed from standard bond distances,[22,24,25] $\boldsymbol{h}$ is Plank's constant, $\boldsymbol{c}$ is the velocity of light, $\boldsymbol{m}$ is the mass of the electron, and $\boldsymbol{N}$ is Avogadro's number. The V_0 values of previously investigated conjugated polyenes[22,24a] varied between 5·3 and 44·5 kcal./mole; in attempting to estimate an upper limit of λ_1 corresponding to the chromophore shown in Fig. 8a, it is assumed that V_0 is 5·3 kcal./mole, whence λ_1 equals 334 mμ. The electronic spectrum of protonated polymer (A) does not show peaks below 470 mμ and it is concluded that the short sequence of conjugated double bonds is not protonated. It follows that the observed effects are due to proton-transfer to the longer sequence; if this contains five * conjugated double bonds, " end-on " protonation would produce the chromophore shown in Fig. 8b. Computing the length L in equation (9) as before,[22,24a] and taking the experimental value of 610 mμ for λ_1, it follows that V_0 is 8·0 kcal./mole. This is reasonable, as shown by comparison with the results of a similar calculation[22] relating to protonated vitamin-A acetate, which also contains five conjugated double bonds.

Polymers (B), (C), (D), *and* (F).—The electronic spectra are somewhat similar to those of polymer (A), and it is probable that the peaks at 250—252 mμ and the peaks or shoulder between 310 and 365 mμ are also brought about by a short and a long sequence of conjugated double bonds. All these polymers are reversible proton-acceptors; the spectra of the protonated species are compatible with the supposition that in all cases the longer sequence of conjugated double bonds reacts with the acid. Confirmation is provided by the equilibrium constants, K, and the ion-pair dissociation constants, K_d, which are of the same order of magnitude as the relevant constants of polymer A.

In the case of free-draining linear-coiling or linear rod-shaped polymers of different molecular weight, M, but comparable chemical structure, the exponent in the relationship, viscosity number ($[\eta]$) = constant × M^α, is either about unity or larger. For four of the five polymers listed in Table 2 log $[\eta]$ is a linear function of log M, within the limits of the experimental error specified. The slope α of the log $[\eta]$–log M graph is $0{\cdot}39 \pm 0{\cdot}07$. It could be suggested that this small α value indicates that these polymers are not free-draining linear species, but this is improbable in view of the small M values. It has been observed[26] that non-linear polymers are characterised by small α values and therefore it is reasonable to assume that the polymers here considered are also non-linear species.

Alternative Interpretation of the Electronic Spectra.—It could be suggested that the double bonds in these polymers are all conjugated and that the observed peaks of the electronic spectra are due to the superposition of the spectra of the various homologues. This, however, is difficult to reconcile[2] with the molecular-weight distribution of polymer A and with the absence of significant influence by the molecular weight on the position of the peaks listed in column 3, and in lines 1, 3, and 5 of column 4, in Table 3.

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

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* This figure, rather than four or six, has been chosen, in view of the proposed mechanism of polymerisation.[2]

[25] Kuhn, *J. Chem. Phys.*, 1949, **17**, 1198.

[26] Zimm and Stockmeyer, *J. Chem. Phys.*, 1949, **17**, 1301; Stockmeyer and Fixman, *Ann. New York Acad. Sci.*, 1953, **57**, 334; Kilb, *J. Polymer Sci.*, 1959, **38**, 403.