883. *Phosphonic Polymers. Part I. The Copolymerisation of Diethyl Vinylphosphonate and Styrene.*

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The monomer reactivity ratios for the copolymerisation of styrene (M_1) and diethyl vinylphosphonate (M_2) have been found to be $r_1 = 3{\cdot}25$ and $r_2 = 0$. The effects exerted by the phosphonic ester group on the course of vinyl polymerisation are discussed in the light of these values.

A study has been made of the relations between the phosphorus content, yield, and intrinsic viscosity of a copolymer and the temperature, initiator concentration, and initial monomer ratio at which it was prepared.

Weight-average molecular weights for a number of the copolymers have been determined by light-scattering measurements, and lie in the range 14,300—55,600.

Copolymers of diethyl vinylphosphonate, $CH_2{:}CH{\cdot}PO(OEt)_2$, and styrene have been prepared, and converted by hydrolysis into the corresponding vinylphosphonic acid–styrene copolymers (I), the properties of which are now being studied. It became clear, in the earlier stages of the investigation, that a quantitative study of the copolymerisation of diethyl vinylphosphonate with styrene was necessary. Accordingly, the reactivity ratios of these monomers have been determined, and relationships between copolymer properties and factors influencing copolymerisation have been ascertained.

$$\cdots\cdots CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}CH(PO_3H_2)\cdots\cdots\cdots CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}CH(PO_3H_2)\cdots\cdots$$

(I)

Monomer Reactivity Ratios.—Styrene and diethyl vinylphosphonate being written as M_1 and M_2, respectively, and radical-chains ending in these units as $M_1^{\cdot}$ and $M_2^{\cdot}$, then, where the rate-constants of the reactions

$$M_1^{\cdot} + M_1 \longrightarrow M_1^{\cdot},\ M_1^{\cdot} + M_2 \longrightarrow M_2^{\cdot},\ M_2^{\cdot} + M_2 \longrightarrow M_2^{\cdot},\ M_2^{\cdot} + M_1 \longrightarrow M_1^{\cdot}$$

are respectively k_{11}, k_{12}, k_{22}, k_{21}, the monomer reactivity ratios, r_1 and r_2, are given by $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$.

The graphical method described by Mayo and Walling [1] has been used.

It is desirable to remove monomers from copolymers prepared for the determination of monomer reactivity ratios by methods which do not involve the separation of fractions of differing composition. Accordingly, copolymerisation initiated by *tert.*-butyl hydroperoxide having been allowed to proceed to about 50% conversion, the monomers were removed by evaporation at reduced pressure, followed by a process in which the solvent was evaporated from a frozen benzene solution of the copolymer, yielding the latter as a porous solid which was finally evaporated to constant weight. Weights and phosphorus contents for four copolymers so prepared are recorded in Table 2; from these data the values $r_1 = 3{\cdot}25$ and $r_2 = 0$ have been calculated. Thus (when the monomers are present in equimolar concentrations) radical-chains $M_1^{\cdot}$ react 3·25 times as frequently with styrene as with diethyl vinylphosphonate, and radical-chains $M_2^{\cdot}$ react only with styrene.

Easy polymerisation of a monomer $CH_2{:}CAX$ is associated with a capacity of the substituent to accommodate a single electron in one or more canonical forms in addition to the form (II). Of the 33 ethylenic monomers whose relative reactivities are tabulated by Mayo and Walling,[1] the 12 most reactive yield radicals of form (III), which is capable of resonance-stabilisation by formation of (IV). The activation energies of initiation and propagation are, presumably, reduced by the contribution which (IV) makes to the transition states in these processes. The formation of a structure analogous to (IV) by the radical (V), derived

$$R^{\cdot} + CH_2{=}CAX \longrightarrow CH_2R{-}\dot{C}AX \quad \text{(II)}$$

$$\text{(III)}\quad CH_2R{-}\dot{C}A{-}CB{=}Y \longleftrightarrow CH_2R{-}CA{=}CB{-}\dot{Y} \quad \text{(IV)}$$

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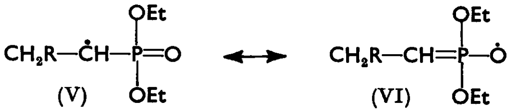
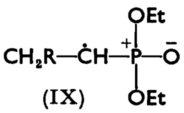
[1] Mayo and Walling, *Chem. Reviews*, 1950, **46**, 191.

from diethyl vinylphosphonate, requires the formation of a carbon–phosphorus double bond (as in VI):



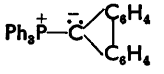
(V) $CH_2R{-}\dot{C}H{-}P(OEt)_2{=}O \longleftrightarrow$ (VI) $CH_2R{-}CH{=}P(OEt)_2{-}\dot{O}$



(IX) $CH_2R{-}\dot{C}H{-}\overset{+}{P}(OEt)_2{-}\bar{O}$

(It can be shown that other forms, in which the single electron is placed on the ethoxyl oxygen, or on phosphorus, all involve a C=P bond.) However, a search has revealed a record of only one compound formulated as containing such a bond, the pentaphenyl compound (VII).[2] The analogous fluorenyl compound (VIII) is formulated by Pinck and Hilbert [3] as a phosphonium zwitterion. It is inferred that there is an obstacle to the formation of carbon–phosphorus double bonds, the nature of which is not discussed here. It follows that the phosphonic ester group is incapable of stabilising, and facilitating the formation of, radical (V) by resonance. [Use of formula (IX), in which oxygen is bonded to phosphorus by a co-ordinate link, does not affect the above conclusion, a C=P double bond again being necessary to render C_α four-covalent.]

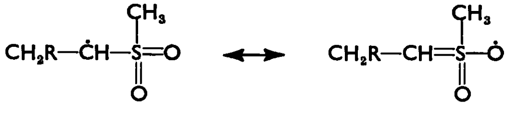
(VII) $Ph_3P{=}CPh_2$



(VIII)

The addition of a molecule of diethyl vinylphosphonate therefore requires attack by a radical of greater than average energy. The radical so formed then reacts, virtually invariably since $r_2 = 0$, with styrene. Inspection of scale models of a diethyl vinylphosphonate radical-chain end, and of diethyl vinylphosphonate monomer, shows that it is sterically possible for the two to approach closely, but that, in the conformations required for such approach, the oxygen atoms of the two phosphonate groups are brought into close proximity. Hence, electrostatic repulsion may oppose reaction between a diethylvinylphosphonate radical-chain end and a molecule of diethyl vinylphosphonate monomer. In addition to this effect, another, tending to the same result, may operate; this arises from the polarisability of monomer molecules, and has been invoked [4, 5] to explain instances of alternate copolymerisation. A radical terminated by the electron-attracting phosphonic ester group may react preferentially with styrene, which bears a phenyl group capable of electron-release of the $+E$ type, rather than with diethyl vinylphosphonate, which bears an electron-attracting substituent.

The values of r_1 and r_2 found for the copolymerisation of styrene and diethyl vinylphosphonate are approximately paralleled by those which have been recorded by Price and Zomlefer,[6] and by Doak,[7] for the copolymerisation of styrene and methyl vinyl sulphone: $r_1 = 2{\cdot}0$, $r_2 = 0{\cdot}01$, and $r_1 = 2{\cdot}4$, $r_2 = 0{\cdot}0$, respectively. If the radical (X), derived from methyl vinyl sulphone, were to be stabilised by resonance with a form analogous to (IV), then the structure (XI) is required. No record has been found of compounds in which carbon is doubly bonded to sulphur when the latter is other than bivalent, whence it is concluded that the bonding of (XI) is improbable, and that the sulphone group is unable to facilitate the formation, or increase the stability, of (X) by contributing the resonance form (XI).



(X) $CH_2R{-}\dot{C}H{-}S(CH_3)(O){=}O \longleftrightarrow CH_2R{-}CH{=}S(CH_3)(O){-}\dot{O}$ (XI)

Factors controlling Copolymerisation.—A study has been made of the relations between the phosphorus content, yield (expressed as conversion of total monomer), and intrinsic viscosity of a copolymer and the temperature, initiator concentration, and initial monomer

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[2] Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 635.

[3] Pinck and Hilbert, *J. Amer. Chem. Soc.*, 1947, **69**, 723.

[4] Bartlett and Nozaki, *ibid.*, 1946, **68**, 1495.

[5] Walling, Briggs, Wolfstirn, and Mayo, *ibid.*, 1948, **70**, 1537.

[6] Price and Zomlefer, *ibid.*, 1950, **72**, 14.

[7] Doak, quoted in ref. 3, but apparently not yet published.

ratio at which it is formed, with the object of delimiting the conditions under which copolymers of given characteristics may be prepared. On the basis of preliminary experiments, there was selected as an " origin " the copolymer formed after 11 hr. at 116° from a mixture of diethyl vinylphosphonate and styrene in molar ratio 1 : 3, containing 1·65% of *tert.*-butyl hydroperoxide; from this point the temperature, initiator concentration, and initial monomer ratio of copolymerisation were varied.

Preliminary experiments had also shown there to be some variation in yield and intrinsic viscosity, but not in phosphorus content, of copolymers prepared under identical conditions from different specimens of diethyl vinylphosphonate. Two complete series of experiments were therefore carried out, both with diethyl vinylphosphonate from one preparation, portions of which were redistilled for each series; the reaction mixtures for each study of a variable (*e.g.*, temperature) were prepared at one time, and heated within a short time of preparation. The removal of monomer by prolonged evaporation, which was used in the determination of monomer reactivity ratios, was replaced in the present experiments by precipitation of the copolymer on addition of its solution in ethyl acetate to methanol. Precipitation necessarily involves a degree of fractionation. There is some removal of copolymer which is relatively high in phosphorus, owing to the circumstance that phosphonic ester groups are more hydrophilic than phenyl groups. Also, copolymer of low molecular weight is removed; a plot of conversion *versus* $[\eta]_c$ for all copolymers shows a relatively abrupt lower termination at $[\eta]_c = 0{\cdot}10$. The reported conversions are, therefore, those to copolymer of molecular weight sufficient to give $[\eta]_c > 0{\cdot}10$.

Intrinsic viscosities, $[\eta]_c$, of 1% solutions of the copolymers in toluene at 25° were determined, and (see p. 4611) do not differ appreciably from the limiting intrinsic viscosities.

The results obtained are recorded in Figs. 1, 2, and 3; the points relating to the " origin " appear in each Figure.

Temperature.—The extent of copolymerisation of diethyl vinylphosphonate, measured by the phosphorus content of the copolymer, varies little with temperature : the phosphorus contents of copolymers prepared at 100°, 116°, and 133° are near 2·6%, those of copolymers prepared at 80° and 154° are somewhat lower. The intrinsic viscosity falls with increase in copolymerisation temperature, and approaches the minimum of 0·10. Conversion attains a maximum at about 112°, then falls rapidly with increasing temperature, the fall being correlated with the approach of the intrinsic viscosity to the minimum value for precipitation.

Initiator Concentration.—Variation in the initial concentration of *tert.*-butyl hydroperoxide over the range 0·75—5·1% has little effect on the phosphorus content of the copolymer, there being a slight fall with increase in catalyst. In both series intrinsic viscosity falls with increase in catalyst; each series is self-consistent, but in the second the values are higher than in the first. Conversion also falls with increase in catalyst, the more marked fall in the first series being correlated with the approach of $[\eta]_c$ to the value 0·10.

TABLE 1. *Weight-average molecular weights of diethyl vinylphosphonate–styrene copolymers.*

Copolymer *	$\overline{W}$	$([\eta]_c/k)^{1/\alpha}$	Copolymer	$\overline{W}$	$([\eta]_c/k)^{1\ \alpha}$
3a	38,500	34,900	16a	36,400	33,400
5b	40,000	35,650	19a	14,700	14,900
6a	29,400	26,100	21a	14,300	14,000
7a	28,200	27,300	27a (i)	28,200	27,500
11b	33,900	34,700	27a (ii)	27,400	27,500
12a	16,000	15,600	28b	55,600	57,300
14a	38,500	38,600	29a	45,400	44,400

* Nos. 3—12, 14—21, 27—29 refer respectively to copolymerisation with initiator, temperature, and monomer-ratio variation, and a and b to the 1st and 2nd series.

Initial Ratio of Monomers.—An increase of 1 to 9 in the molar ratio of styrene to diethyl vinylphosphonate in the initial mixture of monomers resulted in the formation of copolymers containing from 4·5 to 1·5% of phosphorus, equivalent to the presence in the copolymers of 5·0 to 18·6 styrene units per unit of diethyl vinylphosphonate. Intrinsic viscosity (one anomolous value excepted) increases with the styrene content of the copolymers. The conversion into copolymer of molecular weight sufficient for precipitation increases markedly with the styrene content.

Molecular Weights.—The weight-average molecular weights, $\overline{W}$, of a number of the copolymers have been determined (Table 1) by light-scattering measurements, the procedure and method of calculation for which are described in the Experimental section. The values of $\overline{W}$ and $[\eta]_c$ for the copolymers of Table 1 are approximately related by the empirical equation $[\eta]_c = k\overline{W}^{\alpha}$, where $k = 5{\cdot}90 \times 10^{-5}$ and $\alpha = 0{\cdot}7785$, and values of $\overline{W}$ calculated from $[\eta]_c$ by its use are given in Table 1.

FIG. 1.

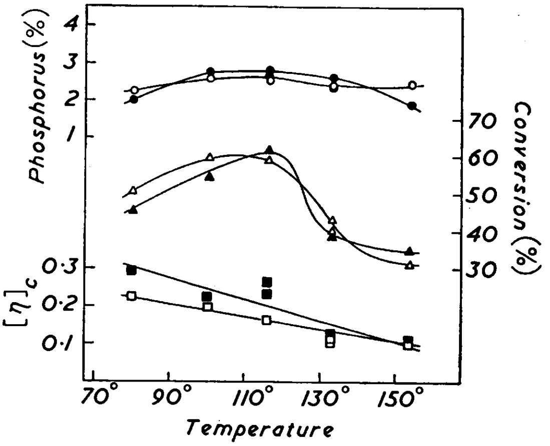


FIG. 2.

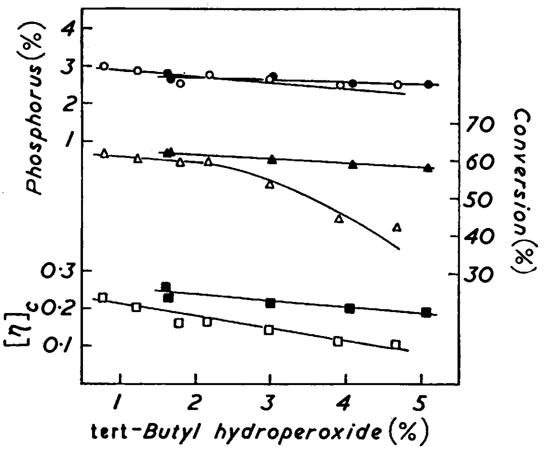
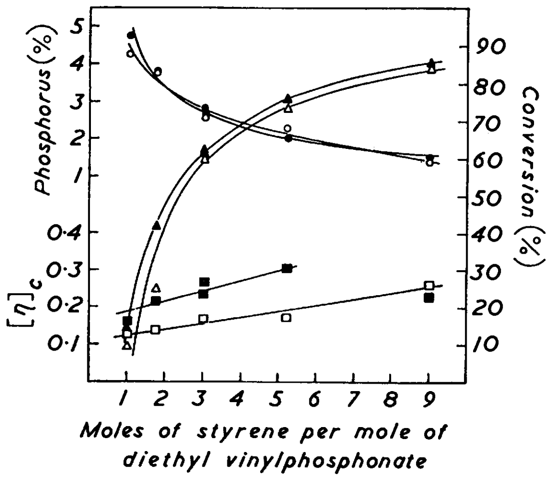


FIG. 3.



Copolymerisation of diethyl vinylphosphonate and styrene.

○ Phosphorus content of copolymer.
△ Conversion of total monomer.
☐ Intrinsic viscosity of copolymer.
" Open " points, first series; " solid " points, second series.

EXPERIMENTAL

Diethyl 2-bromoethylphosphonate was prepared in 58% yield from triethyl phosphite and ethylene bromide, and converted in 87% yield into diethyl vinylphosphonate, by Kosolapoff's methods.[8] Diethyl vinylphosphonate had b. p. 72—75°/2·5 mm., n_D^{25} 1·4262; on hydrogenation, in ethanol with platinum oxide catalyst, it absorbed 100·1% of the calculated quantity of hydrogen.

Styrene was thrice washed with N-sodium hydroxide and thrice with water, dried ($CaCl_2$), and distilled at room temperature under 0·2 mm. pressure, the receiver being cooled in a solid

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[8] Kosolapoff, *J. Amer. Chem. Soc.*, 1948, **70**, 1971.

carbon dioxide–methanol bath. *tert.*-Butyl hydroperoxide was prepared by Davies, Foster, and White's method.[9]

Determination of Monomer Reactivity Ratios.—The quantities of diethyl vinylphosphonate and styrene shown in Table 2 were weighed into the flask *A* (Fig. 4), and *tert.*-butyl hydroperoxide (1% of the weight of monomers) was added. The air in flask *A* was displaced by nitrogen, and the stoppered flask was maintained at 116°, by means of *n*-butanol boiling under reflux in the flask *B*, until it was estimated that 50% of the reaction mixture had polymerised. Flask *A* was then connected, through three traps cooled in solid carbon dioxide–methanol, to a vacuum pump, and the butanol in *B* was replaced by acetone; flask *A* was then kept under 0·5 mm. pressure at 56° until it attained constant weight. Benzene (10 ml.) was added to the contents of *A*; the copolymer dissolved, and the solution was frozen by immersion in solid carbon dioxide–methanol. Flask *A* was then immersed in ice, and the benzene was sublimed at 0·5 mm., yielding the copolymer as a white, highly porous material. It was again kept at 56°/0·5 mm. until it attained constant weight. The total time required for the removal of the monomers by pumping varied from 17 to 227 hr., increasing with the mole-fraction of diethyl vinylphosphonate in the reaction mixture. Phosphorus contents of the copolymers were determined by the method described below, and are recorded, together with the weights of the copolymers, in Table 2.

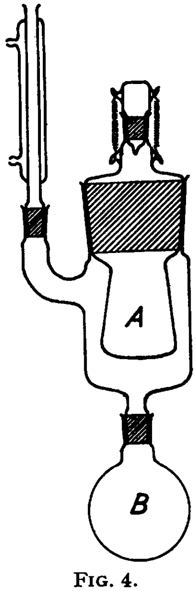

FIG. 4.

Preparation of Copolymers with Variation of Temperature, Initiator Concentration, and Initial Monomer Ratio.—Styrene, diethyl vinylphosphonate, and *tert.*-butyl hydroperoxide, in the proportions given in Figs. 1, 2, and 3 (total quantity 2 g.), were weighed into Pyrex-glass tubes; after displacement of air by nitrogen, the tubes were sealed and heated for 11 hr. in a jacket containing the vapour of one of the following liquids, boiling under reflux at the stated temperature: benzene (80°); water (100°); *n*-butanol (116°); ethylbenzene (133°); anisole (154°). Each tube was then splintered under ethyl acetate (20 ml.), the solution of copolymer was filtered, and the glass residue washed with ethyl acetate (2 × 5 ml.); the filtrate and washings were added slowly with stirring to methanol (225 ml.), residual polymer solution being washed in with a further portion of ethyl acetate (15 ml.). The precipitated copolymer was collected on a sintered-glass crucible, washed with methanol (4 × 50 ml.), dried *in vacuo* (over $CaCl_2$), and weighed. Intrinsic viscosity, weight-average molecular weight by light-scattering, and phosphorus content were determined by the following methods.

TABLE 2.

Copolymer	Styrene (g.)	Diethyl vinylphosphonate (g.)	Copolymer (g.)	P (%)
1	1·8435	0·2102	1·7101	1·10
2	1·3040	0·5069	1·2001	2·86
3	1·1106	0·7573	1·0589	3·64
4	1·0061	1·0497	1·0518	4·88

Intrinsic Viscosity.—The intrinsic viscosity, $[\eta]_c = (1/c) \ln (\eta_{\text{soln.}}/\eta_{\text{solv.}})$, where c = g. of polymer in 100 ml. of solution, of a 1% solution of the copolymer in toluene was determined at 25°. Of selected copolymers, 2% solutions were made, whence 1% and 0·5% solutions were prepared by dilution; their intrinsic viscosities are recorded in Table 3. It is seen that the intrinsic viscosities at $c = 1$ do not differ appreciably from the limiting values implied by the data.

TABLE 3.

Copolymer	c	$[\eta]_c$	Copolymer	c	$[\eta]_c$	Copolymer	c	$[\eta]_c$	Copolymer	c	$[\eta]_c$
8a	2·021	0·150	13b	2·061	0·196	2a	2·082	0·227	29a	2·012	0·254
	1·011	0·149		1·031	0·198		1·041	0·232		1·006	0·262
	0·505	0·149		0·516	0·195		0·521	0·231		0·503	0·264

Molecular Weight by Light-scattering.—Measurements were made with a Brice-Phoenix light-scattering photometer; light of wavelength 546·1 × 10^{-7} cm. from a high-pressure stabilised mercury lamp was used throughout. The solutions for measurement, which were prepared by

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[9] Davies, Foster, and White, *J.*, 1953, 1545.

dilution of a 1% solution of the copolymer in toluene, were filtered under pressure through a No. 5-on-3 sintered-glass filter directly into the photometer cell. Refractive-index differences between solution and solvent were measured in a Rayleigh differential refractometer.

To a good approximation $Hc/\tau = 1/\overline{W} + 2Bc$, where τ is the absolute turbidity, c is the concentration of the solution in g./ml., $\overline{W}$ is the weight-average molecular weight, and B is a constant depending on the solvent; μ_0 being the refractive index of the solvent and μ that of the solution for $\lambda = 546{\cdot}1 \times 10^{-7}$ cm., we have

$$H = 6{\cdot}18 \times 10^{-5} \times \mu_0^2 (\mu - \mu_0)/c^2$$

For each copolymer, values of τ and H were calculated for each solution measured; Hc/τ was then plotted against c, and the intercept on the former axis was equal to the reciprocal of the copolymer weight-average molecular weight.

Determination of Phosphorus.—" AnalaR " inorganic reagents were used. The whole of the copolymer specimen was finely ground by means of a stainless-steel mortar and pestle (the copolymer becomes electrified and scatters in, *e.g.*, an agate mortar). The copolymer (20 mg.), was heated with perchloric acid (72%, 5 ml.) in a small Kjeldahl flask, very gently for 10 min., thereafter more strongly until the solution was boiling; after 30 min. it had become colourless, and heating was continued for a further few minutes until it fumed. Phosphorus was determined as orthophosphate by the following modification of Allen's method.[10]

Amidol (50 g.), in solution in water (125 ml.), was heated with charcoal (1 g.) and filtered; ethanol (100 ml.) was added and the whole was chilled. The colourless crystals of amidol were filtered off, washed with ethanol, and dried *in vacuo*. The reagent solution was prepared daily as follows: to a solution of amidol (1·0 g.) and sodium sulphite ($Na_2SO_3,7H_2O$; 20 g.) in water (60 ml.), sulphuric acid (2·7 ml.) in water (20 ml.) was added. Amidol and the solution were kept in brown glass bottles.

Ammonium molybdate (4·15 g.) was dissolved in water (50 ml.).

The cold perchloric acid solution (above) was diluted with water to 250 ml.; to 25 ml. of this solution were added perchloric acid (72%; 3·5 ml.), amidol reagent (4·5 ml.), and ammonium molybdate solution (3·5 ml.), in that order, and the whole was diluted to 50 ml. with water, and shaken. After 30 min. the absorption of the solution was measured in a Spekker absorptiometer (1 cm. cell; filters having a peak transmittance at 700 mμ), and that of a blank solution of reagents with water was also determined. From the difference (solution reading − blank reading) the phosphorus content was read from a graph (a straight line) plotted from the similarly-determined readings derived from a series of solutions of potassium dihydrogen phosphate.

The oxidative degradation and colorimetric determination were carried out in quadruplicate for the monomer reactivity ratio copolymers, and in duplicate for the copolymers from experiments in which the variables were studied. The arithmetic mean difference between pairs of duplicate determinations was 0·07% of P, and the average difference of one of quadruplicate determinations from the mean of the set was 0·07% of P.

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[10] Allen, *Biochem. J.*, 1940, **34**, 858.