Summary

Mono- and dialkylation of triethyl phosphonoacetate was investigated and several new esters and free acids were isolated. Benzylphosphonoacetic acid was obtained in a state of higher purity than the material reported earlier by Arbuzov and Razumov. The difficulty of securing pure methylphosphonoacetic acid by any of the available methods is discussed. The final link of structure determination of Michaelis' "diacetonephosphinic" acid was achieved.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Polymerization of p-Chlorostyrene in the Presence of Polymethylacrylate. II[1]

BY ROBERT B. CARLIN AND DUANE L. HUFFORD[2]

Preliminary experiments have provided evidence that the polymerization of p-chlorostyrene in the presence of polymethylacrylate produces some polymer molecules in which both p-chlorostyrene and methyl acrylate units are chemically combined.[3] The work reported here was undertaken in an effort to extend and expand the available body of information supporting the postulate that chain branching reactions of the following type may occur in simple vinyl polymerizations.

$$--CH_2CHRCH_2CHRCH_2CHR-- +$$
$$I$$

$$--CH_2CHR'CH_2CHR'\cdot \longrightarrow$$
$$IIa$$

$$--CH_2CHRCH_2\overset{\cdot}{C}CH_2CHR-- +$$
$$\underset{R}{|} \quad Ia$$

$$--CH_2CHR'CH_2CH_2R' \quad (1)$$
$$IIb$$

$$Ia + nCH_2{=}CHR\cdot \longrightarrow$$
$$II$$

$$--CH_2CHRCH_2CRCH_2CHR--$$
$$\left(\begin{matrix} CH_2 \\ | \\ CHR' \end{matrix}\right)$$
$$IIIa \quad \begin{matrix} | \\ CH_2 \\ | \\ CHR' \end{matrix} \quad n{-}1 \longrightarrow \text{Branched polymer (2)}$$
$$III$$

When a pure vinyl monomer polymerizes, reactions such as those formulated above can lead only to branched polymers (III, R = R') which would be extremely difficult to separate and distinguish from the purely linear polymers (I or IIb, R = R'). If, on the other hand, a vinyl monomer (II) is polymerized in the presence of a polymer which is composed of units of a different kind (R ≠ R'), then branched polymers (III, R ≠ R') comprising chains of units of one kind and attached branches formed from units of another kind, might be produced. In the work

described here, as in the preliminary work,[3] p-chlorostyrene (II, R' = p-C6H4Cl) was polymerized in the presence of polymethylacrylate (I, R = COOCH3) at 50°. The polymerizations were carried out in the absence of solvents so that reactions of growing polymer chains (IIa, R' = p-C6H4Cl) with substances other than polymethylacrylate might be minimized. In an effort to discover whether the presence of a polymerization catalyst affects the reaction which produces polymers composed of units of both kinds, 0.7–0.9% of benzoyl peroxide was added to some reaction mixtures but not to others.

After polymerization of p-chlorostyrene in the presence of polymethylacrylate, the products were separated into three fractions by means of a solvent extraction scheme. Methyl acrylate units in the polymers were first hydrolized to acrylic acid units, and polyacrylic acid was separated from the mixture by extraction with water. The water-insoluble polymers were then extracted with benzene until the soluble poly-p-chlorostyrene was removed. Chlorine analyses of the water-soluble and of the benzene-soluble fractions proved that the former contained only traces of poly-p-chlorostyrene and that the latter was essentially pure poly-p-chlorostyrene. The polymer fractions which were insoluble both in water and in benzene were shown by chlorine analyses to possess both p-chlorostyrene and acrylic acid units. For the most part, the units of different kinds must have been present in chemical combination, because intimate physical mixtures prepared from solutions containing both pure p-chlorostyrene and pure polymethylacrylate gave only relatively small amounts of water- and benzene-insoluble fractions when submitted to the separation scheme. The formation of very highly branched poly-p-chlorostyrene, which might be insoluble in benzene and which might thereby complicate the separation scheme, was avoided in all runs by stopping the polymerization of p-chlorostyrene at low conversions.

Experimental

Polymethylacrylate.—Dioxane solutions of the crude polymer[3] were freed of insoluble material, and the polymer was reprecipitated into methanol. After another repre-

(1) Abstracted from a doctor's thesis by Duane L. Hufford; presented before the Organic Division, A. C. S., Philadelphia, Pa., April, 1950.

(2) General Tire and Rubber Co. Fellow, 1947–1949.

(3) Carlin and Shakespeare, THIS JOURNAL, 68, 876 (1946).

TABLE I

Sample no.[a]	Time of pmzn. hr.	Sample wt., g.	Polymer ppt., g.	Conversion, %	"W,"[b] g.	Cl content[e] "W,"[b] %	"WI,"[b] g.	"WI,"[b] extd., g.	'BI-1,"[b] g.	Cl content[e] "BI,"[b] %	"B,"[b] g.	Cl content[e] "B,"[b] %[c]
2Z	0	12.649	1.234	0.90	0.700	0.10	0.142	0.108	0.027	10.15	0.066	24.70
12P	1	13.972	1.435	2.32	.472	.11	.307	.224	.033	12.72	.187	25.59
13P	2	13.356	1.626	3.56	.609	.00	.506	.421	.063	8.94	.344	26.26
5P	3.3	14.884	2.043	5.27	.843	.02	.814	.725	.071	9.42	.629	23.64
3P	4.0	15.285	2.288	5.23	.726	.00	.871	.768	.093	9.14	.654	23.96
7P	5.5	13.972	2.323	8.45	.888	.08	1.125	.975	.088	10.98	.869	24.24
10P	6.5	14.778	2.595	9.47	.486	.05	1.404	1.305	.104	8.79	1.170	25.03
8P	12.5	12.131	3.426	21.21	.278[d]	.06	2.110[d]	1.836[d]	.103[d]	12.38	1.700[d]	25.15
6T	11.5	11.180	1.153	1.52	.502	.20	0.238	0.212	.049	8.83	0.157	24.45
16T	24	13.607	1.562	2.80	.725	.03	.455	.378	.063	12.42	.307	24.30
1T	36	10.645	1.271	3.30	.475	.07	.422	.376	.058	10.25	.302	24.22
15T	48	18.909	2.331	3.73	.618[d]	.10	.648[d]	.566[d]	.070[d]	8.36	.552[d]	24.46
14T	61	10.320	1.764	8.96	.600	.13	.918	.756	.069	10.24	.671	25.04

[a] Z in this column indicates a "zero time" run; P indicates benzoyl peroxide-catalyzed runs; T indicates "thermal" runs. [b] "W" indicates "water-soluble" fraction; "WI" "water-insoluble" fraction; "B" benzene-soluble" fraction; "BI" "benzene-insoluble" fraction. [c] Calcd. for p-chlorostyrene, C_8H_7Cl, 25.61. Low values in this column may be attributed to the difficulty encountered in effecting quantitative ignition of these samples. [d] These values are low because of accidental losses of material. [e] Determined gravimetrically after ignition in the Parr bomb.

cipitation, samples showed reduced viscosities $(\eta_{sp}./c)$ of 0.81–0.92 in 0.1–0.2% solutions in dioxane at 20°.

Polymerization of p-Chlorostyrene in the Presence of Polymethylacrylate.—An 8.93% solution of polymethylacrylate in p-chlorostyrene[3] was prepared by stirring 17.25 g. of the former into 175.8 g. of the latter until the mixture became homogeneous. More concentrated solutions could not be prepared this way, and efforts to concentrate this solution by vacuum evaporation of p-chlorostyrene consumed so much time that extensive polymerization occurred. Attempts to remove dioxane from solutions in it of p-chlorostyrene and polymethylacrylate were abandoned for the same reason.

Chemically-clean glass tubes of approximately 30-ml. capacity were about half filled with the solution, and the remaining space was filled with pure, dry nitrogen. The tubes were cooled in Dry Ice–acetone and sealed under slightly diminished pressure. After predetermined periods of time in a covered thermostat at 50.0 ± 0.5°, tubes were opened, and the contents of each was dissolved in a solution of 100–300 mg. of hydroquinone in 75 ml. of dioxane. The polymer was precipitated into 1 liter of a 1–2% solution of acetic acid in methanol, collected and washed with methanol. These and all other polymer samples encountered in this work were dried at 110–120° in vacuo. The weight of poly-p-chlorostyrene in the sample was computed by subtracting the weight of polymethylacrylate in the charge, minus a correction term of 0.128 g. for the amount of polymethylacrylate which failed to reprecipitate in a control experiment, from the weight of the sample; and the per cent. of monomer converted was calculated from this figure.

Polymer Fractionation.—The dry polymer was stirred overnight with a solution of 4 g. of sodium hydroxide in 100 ml. of ethanol and 100 ml. of distilled water. The solid was separated and stirred with 200 ml. of water until the mixture appeared milky. Any lumps which remained were subjected to the entire procedure again, and the resulting suspension was combined with the original one. After acidification with 5 ml. of concentrated hydrochloric acid, the mixture was concentrated at its boiling point until it could be accommodated within a cylindrical cellophane dialysis membrane (Will Corp.) 28 mm. in diameter by about 18 in. long. Dialysis into distilled water was continued for two days; then the mixture was transferred to a fresh membrane which was suspended in distilled water between a sheet copper cathode and a graphite anode, both 10 cm. square. Electrodialysis (250 volts, 0.05 amp./ sq. dcm.) was continued for four or five days, with occasional manual stirring of the mixture. The aqueous solution inside the membrane then gave no test for chlo-

ride ion, and the water-soluble polymer yielded no more than 0.5% ash. If electrodialysis was not employed, the water-soluble polymer gave as much as 13% ash, and the mixtures contained some non-filterable insoluble polymer, even after several weeks' simple dialysis.

The "water-insoluble" polymer was separated and dried, and the "water-soluble" polymer was isolated from the aqueous solution by replacing the water with 50 ml. of glacial acetic acid and precipitating the polymer from this solution into 500 ml. of ethyl acetate. The "water-insoluble" fraction was ground and extracted in a Soxhlet apparatus with dry benzene for four days, a time interval shown by many preliminary experiments to be sufficient to bring the "benzene-insoluble" portion to constant chlorine content. If enough of this material remained after one chlorine analysis, it was submitted to benzene extraction for another four day period and again analyzed for chlorine. In only one sample did a loss of as much as 4 mg. in weight occur on further extraction, and only in cases where a slight weight loss was accompanied by a significant drop in chlorine content was the result of the second analysis considered to be the true value for the entire sample. In the other cases, the two chlorine analyses were averaged.

The "benzene-soluble" polymer was precipitated from the benzene extracts, after concentration of the latter to 75 ml., into 1 liter of a 2% solution of acetic acid in methanol. The reduced viscosities $(\eta_{sp}./c)$ of two samples which were formed in the presence of benzoyl peroxide were 0.400 and 0.521, in 0.1–0.2% dioxane solutions at 20°; a sample prepared in the absence of benzoyl peroxide under otherwise identical conditions gave a value of 0.912.

Table I summarizes the experimental data for thirteen polymer samples.

Control Experiments.—Pure p-chlorostyrene was distilled into sample tubes, two samples were treated with 100 mg. each of benzoyl peroxide, and the tubes were sealed under nitrogen as previously described. After appropriate periods of time in the thermostat, the tubes were opened and treated with sufficient stock solution, made by dissolving 10.34 g. of polymethylacrylate in 93.2 g. of dioxane, so that the weight ratio of polymethylacrylate to charged p-chlorostyrene was 0.0884. The resulting mixture was treated with 100–300 mg. of hydroquinone, and the solution was diluted to 75 ml. with dioxane. The polymer in the solution was then precipitated and fractionated by means of the procedure described above. For sixteen samples, the average value of the weight of poly-p-chlorostyrene in the "benzene-insoluble" portion was 0.009 ± 0.004 g. No relationships were discernible be-

tween individual values and either per cent. monomer conversion (0–19%) or the presence of benzoyl peroxide. In view of the comparatively constant small magnitude of these values, it appeared likely that this "benzene-insoluble" poly-p-chlorostyrene was the result of the polymerization of small amounts of p-chlorostyrene monomer which adhered to the polymer during its precipitation. Some of this polymerizing monomer would be expected to become bound to polymethylacrylate units, either through chain branching or through depolymerization and repolymerization.[4]

In the water-soluble fractions of the control runs, the weights and chlorine analyses for thirteen samples indicated the presence of 0.001 ± 0.001 g. of poly-p-chlorostyrene in each fraction. The chlorine contents of the "benzene-soluble" fractions were essentially the same as those of similar fractions of the main run.

Calculations.—The weights of poly-p-chlorostyrene in the "water-soluble," "benzene-soluble," and "benzene-insoluble" fractions were calculated from the data in Table I. The value for the "water-soluble" portion was computed simply from the weight of the fraction and the chlorine content. Similar simple calculations could not be used for the other two fractions because of the loss of sample which occurred in removing the "water-insoluble" polymer from the vessel in which it was dried. To compensate for this loss, the weight of poly-p-chlorostyrene found in the "benzene-insoluble" fraction, obtained from the weight of the fraction and its chlorine content, was multiplied by the correction factor: (weight of "water-insoluble" material)/(weight of "water-insoluble" polymer extracted). The correction factor is the value in Column 8 divided by the value in Column 9, Table I, for each sample. The application of this factor involves the undoubtedly erroneous assumption that the portion of the "water-insoluble" fraction lost has the same composition as the entire original fraction, but the magnitude of the error is probably smaller than that which would be introduced if no correction for the weight loss were applied.

If the weights of poly-p-chlorostyrene in the "benzene-soluble" fractions were to be calculated from the respective sample weights and chlorine analyses, then both the correction factor defined in the preceding paragraph and a second correction factor for the solubility of the sample in the precipitating medium would have to be applied. Instead, the total weight of "benzene-insoluble" polymer was computed by multiplying the observed weight by the "water-insoluble loss correction factor," and this value was subtracted from the weight of the "water-insoluble" fraction (Column 8, Table I) to give the weight of the "benzene-soluble" fraction. From this and the observed chlorine content (final column, Table I), the weight of poly-p-chlorostyrene in this fraction was obtained.

In Table II, the weights of poly-p-chlorostyrene calculated for each fraction are shown for each sample. The sum of these values appears under the heading "Total Poly-p-chlorostyrene Calculated." For purposes of comparison, the "Total Poly-p-chlorostyrene Found" by subtracting the calculated weight of polymethylacrylate from the weight of polymer precipitated (Column 4, Table I) is given in the final column.

Results and Discussion

The per cent. of total poly-p-chlorostyrene which combined chemically with polymethylacrylate during polymerization at 50° has been calculated for each sample. Column 3, Table III gives these values, which were obtained by subtracting correction terms for the "benzene-insoluble" plus "water-soluble" poly-p-chlorostyrene in the control runs and in the "zero time" run (2Z) from the sum of the weights of poly-p-

(4) Mesrobian and Tobolsky, THIS JOURNAL, **67**, 785 (1945); *J. Polymer Sci.*, **2**, 463 (1947); Taylor and Tobolsky, THIS JOURNAL, **67**, 2063 (1945).

DISTRIBUTION OF POLY-p-CHLOROSTYRENE AMONG POLYMER FRACTIONS

	PPCS[a] in			Total PPCS[a]	
Sample	Water sol.	Benzene insol.	Benzene sol.	Calcd.	Found
2Z	0.003	0.014	0.102	0.119	0.104
12P	.002	.022	.261	.285	.298
13P	.000	.023	.439	.462	.433
5P	.001	.029	.675	.705	.714
3P	.000	.037	.713	.750	.800
7P	.002	.041	.966	1.009	1.075
10P	.001	.037	1.217	1.308	1.275
8P	.001	.052[b]	2.000[b]	2.053[b]	2.343
6T	.004	.019	0.186	0.209	0.155
16T	.001	.036	.396	.433	.347
1T	.001	.024	.372	.397	.320
15T	.003	.033[b]	.586[b]	.622[b]	.642
14T	.003	.033	.869	.905	.842

[a] Indicates Wt. (g) of poly-p-chlorostyrene. [b] These values are low because of accidental losses of material.

chlorostyrene in the "benzene-insoluble" and "water-soluble" fractions for each sample (Columns 2 and 3, Table II). Table III also gives the per cent. of the p-chlorostyrene monomer charged into each sample which ultimately became bound to polymethylacrylate, on polymerization at 50°. These figures, listed in Column 4, have also been corrected for "zero time" and control runs. Similarly, the figures in Column 2 have been corrected for "zero time" conversion.

POLY-p-CHLOROSTYRENE COMBINED WITH POLYMETHYLACRYLATE

Sample	Conversion, %	Combined PPCS,[a] %	Charged PCS[b] combined, %
12P	1.4	1.4	0.02
13P	2.7	0.63	.02
3P	4.4	2.3	.10
5P	4.4	1.4	.06
7P	7.6	2.2	.17
10P	8.6	1.4	.12
8P	20.4	1.7	.35
6T	0.62	8.1	.05
16T	1.9	8.0	.16
1T	2.4	3.9	.09
15T	3.5	2.7	.09
14T	8.1	2.7	.21

[a] Indicates poly-p-chlorostyrene. [b] Indicates p-chlorostyrene.

Because of the number of mechanical operations to which each sample was subjected during the course of its fractionation and analyses of the three fractions, and because of the errors in the correction factors which were required in the calculations, the values in the third and fourth columns of Table III are subject to appreciable uncertainties. In view of the reasonably good agreement between calculated and found total poly-p-chlorostyrene (Columns 5 and 6, Table II), these Table III values can hardly be in error

by margins greater than ±1% and ±0.05%, respectively. While such margins of error serve to eliminate the data in Table III from use in quantitative evaluations, they are not sufficient to mask some clearly discernible qualitative trends.

The increasing trend in the figures in the right-most column of Table III with increasing monomer conversion shows that p-chlorostyrene units continue to become attached to polymethylacrylate chains as polymerization progresses, in accordance with expectations. Reference to the third column of Table III discloses that, of the p-chlorostyrene which polymerizes, a larger fraction combines with polymethylacrylate when no catalyst is added to the reaction mixtures. In addition, this fraction decreases with increasing per cent. of monomer polymerized in the "thermal" polymerizations. In the peroxide-catalyzed runs, the fractions of combined poly-p-chlorostyrene are of about the same magnitude as the probable error, so that no trend can be detected.

The decrease in the fraction of combined poly-p-chlorostyrene at corresponding monomer conversions caused by the presence of benzoyl peroxide may be interpreted readily in terms of chain branching reactions of the type represented by equations 1 and 2. Application of currently accepted theories of free radical induced vinyl polymerization to the chain branching mechanism leads to the conclusion that the rate of entry of p-chlorostyrene into combination with polymethylacrylate, measured as a function of monomer conversion, should be proportional to the

ratio of free radicals which have polymethylacrylate chains within the "free radical molecules" (e.g., IIIa, R = $COOCH_3$, R' = p-C_6H_4Cl) to total free radicals. An inverse relationship between this ratio and total free radical concentration can be derived; therefore, the introduction of benzoyl peroxide, which increases the total free radical concentration, should have the effect of reducing the ratio and with it the fraction of poly-p-chlorostyrene combined with polymethylacrylate.

Summary

The polymerization of p-chlorostyrene in the presence of polymethylacrylate gives polymers each of which, after saponification and dialysis, may be divided into three fractions on the basis of their solubility behavior in benzene and in water. Control runs, in which solutions of separately polymerized poly-p-chlorostyrene and polymethylacrylate are subjected to the same procedures, give relatively small amounts of fractions insoluble both in benzene and in water; therefore, the greater portions of such fractions formed in the "normal" runs must be the result of chemical interaction between p-chlorostyrene and polymethylacrylate. The experimental observations may be explained by assuming that growing poly-p-chlorostyrene chains undergo free radical chain transfer reactions with polymethylacrylate, with the result that polymer molecules consisting of polymethylacrylate chains having poly-p-chlorostyrene branches are formed.

Electrokinetics of Hydrogen Evolution. I. Hydrogen Overvoltage on Mercury[1]

BY BENJAMIN POST AND C. F. HISKEY.

In this paper measurements of hydrogen overvoltage on mercury cathodes, in ordinary water, are presented and discussed. In a second paper measurements made in heavy water will be reported and compared with the above.

In 1905 Tafel[2] made the important observation that the overvoltage varied with the current density and that the relation could be expressed by an equation of the form

$$\eta = a + b \log i$$

where η is the overvoltage, a and b are constants, and i is the current density. Much of the experimental work in this field since that time has been

concerned with the determination of the values of a and b for a number of electrodes.

There is little agreement among the published results. In Fig. 1 are shown sets of typical measurements of hydrogen overvoltage on mercury cathodes at room temperature.

There is a similar lack of agreement concerning the nature and magnitude of the variation of overvoltage with temperature. Bowden's measurements[3] were long accepted as correct, but the results of recent investigations by Jofa and co-workers[4,5] and by Bockris and Parsons[6] differ significantly both from Bowden's results and from each other.

In this investigation efforts were first concen-

(2) J. Tafel, Z. physik. Chem., 50, 641 (1905).

(3) F. P. Bowden, Proc. Roy. Soc. (London), 126a, 107 (1929).

(4) Z. A. Jofa and K. P. Mikulin, J. Phys. Chem. U. S. S. R., 18, 137 (1944).

(5) Z. A. Jofa and V. Stepanova, ibid., 19, 125 (1945).

(6) J. O'M. Bockris and R. Parsons, Trans. Faraday Soc., 45, 416 (1949).