ticle size or that this particle represents the chemical molecule rather than an aggregate. This investigation indicates the possibility of further work on the natural state of glycogen, methods of its preparation and the interpretation of experimental results on inhomogeneous systems in general.

MADISON, WISCONSIN   RECEIVED JUNE 29, 1942

The Structure of Copolymers of Vinyl Chloride and Vinyl Acetate[1]

BY C. S. MARVEL, GIFFIN D. JONES, T. W. MASTIN AND G. L. SCHERTZ

It is widely recognized that the simultaneous polymerization of two monomers in a mixture leads to products that are quite different from the mixtures obtained by polymerizing the two monomers separately and then combining the polymers. The copolymerization of the monomers thus must lead to mixed units of two monomers in a single polymer chain.

Considerable experimental evidence supporting this generally accepted fact can be cited. Hill, Lewis and Simonsen[2] have made copolymers of butadiene and methyl methacrylate and then ozonized them. The ozonolysis products were such as to show that in general the methyl methacrylate units were sandwiched between butadiene units and that the latter were usually attached by the 1 and 4 carbon atoms in the chain. There was also evidence of direct union between butadiene units and between methyl methacrylate units in the polymer chain. Thus in this particular case almost every possible type of union between the monomers seems to have occurred when the mixture of monomers was polymerized.

Staudinger,[3] Norrish,[4] and others[5] have shown by their studies of copolymers of styrene and p-divinylbenzene that cross-linking of chains occurs due to the participation of the divinylbenzene in the reaction. Hence real copolymers must form.

Staudinger and Schneiders[6] have shown that a copolymer of vinyl chloride and vinyl acetate can be separated into products containing varying amounts of chlorine by means of fractional precipitation. This suggests considerable non-homogeneity of product.

Previous work in this Laboratory has shown that vinyl chloride when polymerized alone gives a 1,3 product[7] and likewise when vinyl acetate alone polymerizes,[8] a 1,3 product results. The present work on the copolymers of these two compounds was undertaken to see whether the two monomers entered the copolymer chains in the same arrangement. The first samples examined were some high-chlorine experimental "Vinylites" prepared in the research laboratories of Carbide and Carbon Chemicals Corporation and furnished to us with that Company's permission by Dr. G. H. Young at Mellon Institute. An attempt was made to study the distribution of chlorine in the polymer chain by statistical methods using the dehalogenation of the polymer by zinc.[7] The results of these experiments seemed to be what was expected for a chance distribution in the polymer chains of vinyl chloride and vinyl acetate units.[9]

Next an attempt was made to apply the same procedure to some low-chlorine vinyl chloride-vinyl acetate copolymers made in our own Laboratory. In early results we found the chlorine was removed in far greater quantities than should have been the case if the vinyl chloride units were distributed in the polymer chains according to chance alone. The dehalogenation experiments did not prove to be too satisfactory and were, in fact, not readily reproducible but they did prove that the chlorine atoms were closer together than chance alone would explain.

At this stage of our work, Wall[10] pointed out that two monomers may have quite different tendencies to enter the growing chain of the copolymer. If the two monomers do enter the chain at different rates the polymer found will not have a uniform composition. Wall's equation[10] can be used to express this relation. When α is 1, the

(1) This paper was first presented at the Gibson Island Conference on Polymers in July, 1941, and it is the fourteenth communication on the structure of vinyl polymers. For the thirteenth see THIS JOURNAL, **64**, 1675 (1942).

(2) Hill, Lewis and Simonsen, *Trans. Faraday Soc.*, **35**, 1073 (1939).

(3) Staudinger, *ibid.*, **32**, 323 (1936).

(4) Norrish and Brookman, *Proc. Roy. Soc.* (London), **163A**, 205 (1937).

(5) Blaikie and Crozier, *Ind. Eng. Chem.*, **28**, 1155 (1936).

(6) Staudinger and Schneiders, *Ann.*, **541**, 151 (1939).

(7) Marvel, Sample and Roy, THIS JOURNAL, **61**, 3241 (1939).

(8) Marvel and Denoon, *ibid.*, **60**, 1045 (1938).

(9) Wall, *ibid.*, **62**, 803 (1940); *ibid.*, **63**, 821 (1941).

(10) Wall, *ibid.*, **63**, 1862 (1941).

$$\frac{dn_x}{dn_y} = \alpha \frac{n_x}{n_y}$$

two monomers enter the chain at the same rate and the polymer formed at any instant will be of the same composition as the mixture of monomers from which it is produced.

Since our low chlorine copolymer of vinyl chloride and vinyl acetate lost more chlorine than was expected when treated with zinc, it was thought that the α value for this pair of monomers was probably not unity for the experimental conditions used in preparing the samples studied. To test this we ran some interrupted polymerizations to see how the chlorine content of the growing copolymers change. A wide variety of mixtures of vinyl chloride and vinyl acetate were prepared. These mixtures were polymerized under different conditions and for different lengths of time. The complete details are recorded in the experimental part but one example here shows the general trend. A mixture of vinyl chloride and vinyl acetate containing 12.48% of chlorine was divided into four sealed tubes. A little benzoyl peroxide was added and the tubes were allowed to stand for various times. The tubes were opened and the polymers isolated. The molecular weights of the polymers formed at different stages were not markedly different as indicated by viscosity measurements. The tube opened first gave a 49% yield of a copolymer containing 17.65% of chlorine; the second tube gave a yield of 65% containing 15.08% of chlorine; the third tube gave a yield of 78% containing 13.90% of chlorine and the last tube gave a 95% yield of polymer containing 12.48% of chlorine. It is thus obvious that vinyl chloride enters the polymer chain much more rapidly than does vinyl acetate when these two monomers are copolymerized from a mixture. It is also obvious that each polymer chain laid down from this mixture is probably different from every other one, for as the composition of the monomer changes, the ratio of units which enter the polymer will change.

From the examination of a wide variety of copolymerization mixtures of vinyl chloride and vinyl acetate the value of α in Wall's equation at 40° seems to be between 1.5 and 2 and the ratio seems to approach 1 as the temperature of the polymerization is increased.

Once these facts were established, it was clear that the suggestion contained in certain patents[11]

that copolymers of improved uniformity could be obtained by the addition of portions of one constituent during the polymerization was based on information of the same sort which we have rediscovered.

Likewise, it has been shown in other cases that the composition of a copolymer is not necessarily related to the composition of the monomer mixture from which it is produced. Thus, in a thorough study of copolymers of vinylidene chloride, it has been found that in general, vinylidene chloride enters the growing polymer chain faster than do vinyl esters,[12] various esters of allyl alcohol derivatives[13] and vinyl ethers.[14] In the case of the copolymers of vinylidene chloride and the acrylate esters, temperature appears to be an impoitant factor since at 45° vinylidene chloride enters the chain faster than ethyl acrylate, whereas at 30° methyl methacrylate and methyl acrylate enter the growing chains more rapidly than does vinylidene chloride.[15] In the case of copolymers of styrene and vinylidene chloride, a copolymer containing 60% by weight of styrene has been obtained from a monomer mixture containing about 30% by weight of styrene.[15]

Further experiments on the removal of chlorine from copolymers of vinyl chloride and vinyl acetate have yielded results which are not as readily reproducible as would be desired. Yet they are of interest when compared with the statistical calculations made by Wall.[9,10]

In Fig. 1 we have reproduced certain curves which Wall has published[9,10] and have superimposed on them certain points which were arrived at by averaging the results of many dehalogenation experiments on different copolymers. While the degree of accuracy of the dehalogenation is not all that one may desire yet the apparent trend is for these points to follow the curves based on a "head to tail" arrangement of the monomer unit in the chain.

The dehalogenated product did not decolorize a dilute solution of potassium permanganate in acetone but did decolorize a solution of bromine in carbon tetrachloride. These reactions indicate that dehalogenation may have produced cyclopropane units in the chain and do not indicate an

(11) Johnson, British Patent 467,084 (C. A., 31, 8077 (1937)).

(12) Wiley, U. S. Patent 2,160,931 (C. A., 33, 7443 (1939)).

(13) Britton, Davis and Taylor, U. S. Patents 2,160,940, 2,160,941, 2,160,942 (C. A., 33, 7441 (1939)); Britton and Taylor, U. S. Patent 2,160,946 (C. A., 33, 7442 (1939)).

(14) Britton and Davis, U. S. Patent 2,160,943 (C. A., 33, 7442 (1939)).

(15) Wiley, U. S. Patent 2,160,932 (C. A., 33, 7443 (1939)).

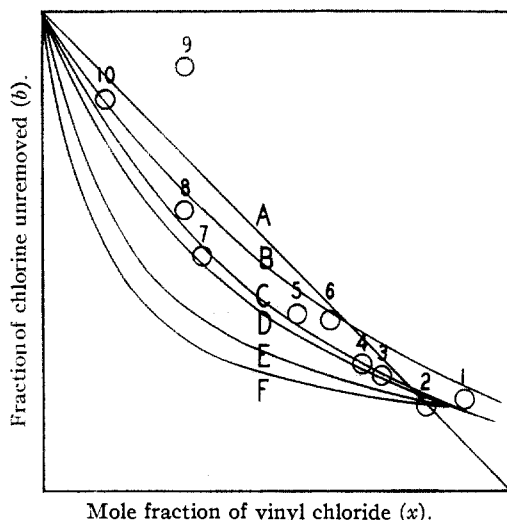Mole fraction of vinyl chloride (x).

Fig. 1.—A, $f = 1 - x$ "head to head" arrangement of monomer units; B, $f = e^{-x}(1 - (x/2))$ random arrangement of monomer units; C, $f = e^{-2x}$ "head to tail" arrangement of monomer units, $\alpha = 1$; D, $f = \left(\dfrac{R+2}{2}\right)^2 e^{-4/(2-R)} - \left(\dfrac{R}{2}\right)^2$, where R is the ratio of vinyl acetate to vinyl chloride in the completed polymer and $\alpha = 2$; E, f as function of x for $\alpha = 5$; F, f as a function of x for $\alpha = 10$.

olefin structure. Further evidence of the absence of 1,2-chlorine atoms was the fact that no iodine was produced when a sample of "Vinylite" was refluxed in acetone with potassium iodide.

Careful hydrolysis of a copolymer of vinyl acetate and vinyl chloride by treating the ester with water, ethyl alcohol and hydrochloric acid in dioxane solution has given the chlorohydrin.[16] This product is not oxidized by periodic acid. The best available evidence thus indicates that the vinyl chloride and the vinyl acetate enter the copolymer chain to give "head and tail" units just as they do when polymerizing alone. The fact that the chlorohydrin is actually obtained is further proof that a real copolymer is in hand and that the reaction does not merely produce mixtures of individual polymers.

The relative homogeneity of some of these copolymers has been further tested by solubility methods. 1-Heptyne will dissolve polyvinyl acetate[17] but does not dissolve "Vinylite." Phenylacetylene will dissolve low-chlorine "Vinylites" but will not dissolve high-chlorine "Vinylites" or polyvinyl chloride. Mixtures of polyvinyl acetate, polyvinyl chloride and the copolymer were

(16) The hydrolysis of such a copolymer by means of sulfuric acid, alcohol or benzene has been reported in French Patent 724,910 (1931).

(17) Marvel, Harkema and Copley, THIS JOURNAL, **63**, 1609 (1941).

separated into different fractions but due to the non-homogeneity of the copolymer the separation was not 100%. These solubility experiments showed that none of the copolymers tested in this work was strictly homogeneous.

It should be pointed out that most of the molecular weights reported in this manuscript were determined by viscosity methods and are, therefore, only of relative value. Since the results of Staudinger and Schneiders[6] do not permit an unequivocal choice of a K_m for "Vinylite" in dioxane solution and since viscosity molecular weights are of comparative significance only, an approximate K_m value was used in this work. This value was obtained by determining the viscosity of a single polymer in dioxane and in methyl n-propyl ketone. Douglas and Stoops[18] have determined that K_m has the value 3.2×10^{-4} for "Vinylites" in ketone solvents. Our comparisons indicated a value 4.1 $\times 10^{-4}$ would be an approximate K_m in dioxane.

Experimental

Molecular Weight Determination.—All molecular weights were obtained by making viscosity measurements on solutions containing 0.1 g. of polymer in 50 cc. of pure dioxane at 20° in an Ostwald viscometer, and then calculating the molecular weight by the Staudinger equation using the K_m value 4.1×10^{-4}. This value was ascertained by determining the relative viscosities of a given polymer in dioxane and in methyl propyl ketone. Only this one experiment is recorded in detail.

An experimental "Vinylite" containing 37.7% chlorine was used. The following results were obtained at 20° using a 5-cc. Ostwald viscometer.

Liquid	Time in seconds
Pure dioxane	122.2 122.6 122.5
0.10 g. of polymer in 10 cc. of dioxane	132.2 133.2 132.5 132.2
0.10 g. of polymer in 10 cc. of dioxane	131.2 132.3 132.8 132.8
Pure methyl n-propyl ketone	65.5 65.5 65.1 65.1 65.3
0.10 g. of polymer in 10 cc. of methyl n-propyl ketone	69.5 69.5
0.10 g. of polymer in 10 cc. of methyl n-propyl ketone	69.5 69.6

$\eta_{rel.}$ in dioxane 1.0817; $\eta_{rel.}$ in methyl n-propyl ketone 1.064

$$\frac{\eta_{rel.} - 1}{K_m C} = M = \frac{\eta_{rel.} - 1}{K_m C}$$

(dioxane)   (methyl n-propyl ketone)

$$\frac{0.0817}{K_m(\text{dioxane})} = \frac{0.064}{3.2 \times 10}$$

K_m (dioxane) $= 4.08 \times 10^{-4}$.

This figure was rounded off to 4.1×10^{-4} for further use.

(18) Douglas and Stoops, Ind. Eng. Chem., **28**, 1152 (1936).

<div align="center">TABLE I</div>

<div align="center">PREPARATION AND PROPERTIES OF LOW-CHLORINE COPOLYMERS OF VINYL CHLORIDE AND VINYL ACETATE</div>

Vinyl chloride	Reagents used, g. Vinyl acetate	Benzoyl peroxide	Time of experiment in hr.	Yield of product, g.	Chlorine,[20] %	Mol. wt. (viscosity)
0.86	3.06	0.03	63	3.72	12.48	14,000
2.53	2.24	none	100	3.82	30.2	8,100
3.45	4.79	0.03	100	7.29	23.9	14,000
1.27	3.85	none	70	4.17	13.7	21,000
1.10	2.97	0.03	40	3.20	15.4	12,000

Higher Chlorine Copolymers.—Four experimental "Vinylites"[19] containing 87, 77, 65 and 60% vinyl chloride, respectively, were used in the early part of this work. These polymers were white powders which softened at about 110° and were reported to have molecular weights in the range of 28,000. Chlorine analyses in our Laboratory confirmed the compositions reported. In the interrupted polymerizations reported later in this manuscript a few other high-chlorine "Vinylites" were obtained.

Low-Chlorine Copolymers.—Copolymers containing less than 50 mole per cent. of vinyl chloride (42% vinyl chloride or 23.9% chlorine) were prepared by adding freshly distilled vinyl acetate to liquefied vinyl chloride and adding a small amount of benzoyl peroxide ("Lucidol"). The mixture was cooled in dry-ice and sealed in a glass tube. The mixture was allowed to come to room temperature and in most cases irradiated with ultraviolet light at about 40°. The tubes were usually exposed at this temperature for about thirty hours or until they contained a milky opaque solid. Longer exposure to ultraviolet light gave deeply colored products.

After polymerization had apparently stopped, the tubes were opened and the contents dissolved in dioxane to give a solution containing from 0.5 to 2% of polymer. The lower concentrations were used for the lower chlorine polymers. This solution was then aspirated in a fine spray on the surface of vigorously stirred running water. The outfit used is shown in the diagram (Fig. 2). The right-hand tube carried water and the left-hand tube compressed air. Only in this way could low-chlorine copolymers be isolated as solids which could be handled. The precipitation of one lot of polymer usually required about eight hours per liter of dioxane solution. The polymer which was collected in the filter cloth was dried by squeezing out most of the water and then heating at 55° (boiling acetone) in a drying pistol over phosphorus pentoxide at about 20 mm. until the weight was constant.

Copolymers having more than 10% chlorine can be isolated easily as fluffy powders by this method. Copolymers with less than 10% chlorine are very hard to get in a powdery form. They adhere together in a tough mass but these tough masses seem to give constant analyses if carefully dried.

Table I shows the results of some of these experiments. All the experiments were carried out at 40°.

Interrupted Polymerizations.—Various mixtures of vinyl chloride and vinyl acetate containing benzoyl peroxide were prepared and divided into tubes. The mixtures

were allowed to polymerize for various lengths of time and then the polymer isolated as above and examined. In other cases a solution of vinyl chloride and vinyl acetate of known chlorine content was allowed to polymerize for a certain period and then the polymer isolated to determine the yield and chlorine content. Other experiments were made with solutions and emulsions. In every case where polymerization was stopped before the yield of polymer was essentially quantitative the polymer contained a higher percentage of chlorine than had been present in the original polymerization mixture. The results of these experiments are summarized in Table II.

Dehalogenation Experiments on "Vinylites."—In general, the zinc dehalogenation experiments were carried out as described previously[7] except that the solutions were only one-half as concentrated in this work. Usually, 0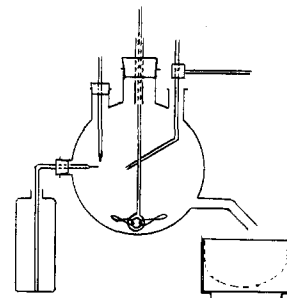.2 g. of polymer was dissolved in 50 cc. of dioxane. In some runs large amounts of solute and solvent were used but this ratio was always maintained. That boiling alone did not affect the polymer was shown by refluxing a sample of "Vinylite" having 26.5% chlorine and a molecular weight of 17,000 for five days in dioxane. After isolation of the polymer the molecular weight was found to be 17,000 and the chlorine content 25.9%.

Fig. 2.—Apparatus.

Boiling a "Vinylite" sample (1 g.) having 15.4% chlorine in dioxane (750 cc.) containing 0.148 g. of zinc chloride for five days gave a red-brown solution. On isolation the polymer contained only 9.18% chlorine after this treatment. In a similar experiment the following analyses before and after treatment, respectively, were obtained: C, 48.3; H, 6.23; Cl, 23.9; and C, 52.8; H, 5.8; Cl, 15.0.

These experiments indicate that dehalogenation by zinc may be accompanied by other reactions which account for the erratic results in some experiments recorded in Table III.

No evidence that acetate groups were removed by the zinc treatment was obtained by applying the lanthanum nitrate test[21] or by comparing the analyses of the polymer before and after the treatment.

There is some indication that the dehalogenation does not cause as much degradation and side reaction as does the zinc chloride treatment. For example, in the zinc

(19) These were obtained from Carbide and Carbon Chemical Corp. through the courtesy of Dr. G. H. Young of Mellon Institute. We are grateful to Dr. Young and to the Carbide and Carbon Chemicals Corp. for their aid.

(20) Analyses by Parr bomb fusion, followed by Volhard titration.
(21) Reedy, "Elementary Qualitative Analysis," 3rd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

TABLE II
RESULTS OF SOME INTERRUPTED POLYMERIZATION EXPERIMENTS

Expt.	Chlorine content mixture, %	Conditions of polymerization	Time, hr.	Yield of polymer, %	Chlorine content of polymer, %	Mol. wt. (viscosity method)	α Wall's equation
7.1	12.48[a]	Peroxide,	24	49	17.65	9,900	2.24
7.2		light, 40°	28	65	15.08	17,000	1.81
7.3			33	78	13.90	12,000	1.83
7.4			63	95	12.48	14,000	
8.1	30.2[a]	Light, 40°	23	3.4	37.4		1.73
8.2			30	26	37.3	7,600	1.83
8.3			14	16	35.3	8,600	1.49
8.4			100	80	30.2	8,100	
11	34.1	Light, 40°	15	5.6	42.4	7,600	2.01
13	47.7	Peroxide, 60°	120	53	49.3	8,600	1.41
14.1	15.4[a]	Light, 40° emulsion	24	16	33.9	7,600	4.80
14.2			23	17	33.4	10,000	4.65
14.3			31	56	13.4	11,000	0.74
14.4			62	79	15.4	12,000	
15.1	26.0[a]	Light, peroxide, 40° soln.	33	51	30.0	3,500	1.56
15.2			34	66	26.9	1,900	1.14
15.3			82	82	26.0	3,800	
17.1	26.1[a]	Light, 18°	71	11	38.5	18,000	2.47
17.2		peroxide 80°	25	. .	33.2	4,100	1.62
17.3		40°		90	26.1	14,000	
20.2	10.13[a]	Peroxide 122°	12	26	14.6	5,000	1.77
20.4		135°	6	26	14.4	4,500	1.73
20.5		149°	6	25	12.0	4,400	1.12
20.1		Light 40°	48	90	10.13	46,000	
19	17.9	Peroxide 123°	10.5	25	21.6	3,800	1.37

5% tetrapropyl tin added

[a] Inferred from composition of polymer in completely polymerized case.

TABLE III
DEHALOGENATION EXPERIMENTS WITH VARIOUS EXPERIMENTAL "VINYLITE" SAMPLES

	Description of polymer used		% yield (where not complete polym.)	Fraction chlorine remaining	Calcd. fraction For 1,3-arrangement, $\alpha = 2$	Random arrangement
% Cl	% vinyl Cl	Mole fraction vinyl Cl				
49.4	87	0.905		0.198	0.163	0.221
43.7	77	.823		.193	.190	.260
36.9	65	.718		.242	.230	.311
34.1	60	.674		.278	.250	.338
21.0	36.9	.447		.290	.377	.497
13.2	23.25	.302		.409	.502	.628
11.7	20.65	.260		.320	.548	.671
5.85	10.3	.137		.820	.720	.812
15.08	26.5	.332	65	.863	.473	.599
37.4	65.8	.726	3.4	.216	.229	.308
37.3	65.7	.725	26	.205	.229	.308
35.3	62.2	.693	16	.216	.241	.327
30.2	53.2	.611	80	.305	.280	.377
43.2	76.0	.813	53	.160	.194	.263
23.9	42.1	.499	89	.307	.344	.456
42.4	74.7	.802	5.6	.106	.198	.268
13.7	24.1	.304	82	.891	.500	.626
49.3	86.9	.901	53	.138	.163	.223
33.9	59.7	.670	16	.503	.250	.341
33.4	58.8	.663	17	.144	.255	.345
13.4	23.6	.297	56	.589	.508	.632
15.4	27.1	.339	79	.494	.476	.592
30.0	52.8	607	51	.237	.282	.380
26.9	47.4	.553	66	.362	.312	.416
26.0	45.8	.537	82	.372	.321	.428

TABLE IV

SOLVENT FRACTIONATION OF COPOLYMERS OF VINYL CHLORIDE AND VINYL ACETATE

Copolymer, g.	% Chloride in copolymers	Mol. wt. (viscosity)	Extracted by 1-heptyne, g.	% Chlorine	Extracted by phenyl-acetylene, g.	% Chlorine	Insoluble fraction, g.	% Chlorine
1.984	47.5	4,500	0.195	..	0.627	35.8	1.611	47.9
2.003	36.9	13,000	.286	..	1.947	23.6	0.851	47.4
2.282	49.3	8,600	.088	..	0.394	..	2.059	48.6
2.226	25.0	3,800	.800	14.4	1.576	29.8	trace	
1.741	30.0	3,500	.220	26.4	1.487	30.7	trace	

chloride treatment, the solution becomes red, but the dehalogenation solution does not; also the color of the former solution is destroyed by refluxing an hour with zinc. Furthermore, analyses indicate that loss of chlorine is the major result of the dehalogenation treatment. For example, a polymer which had been 35% dehalogenated (the dehalogenation was incomplete, since the theory would have predicted 65% removal) had the composition before treatment: C, 47.45; H, 5.83; Cl, 27 (ratio, C:H:Cl:O = 1.00:1.46:0.193:0.312) and after treatment: C, 52.9; H, 6.5; Cl, 17.5; (ratio: C:H:Cl:O = 1.00:1.46:0.112:0.328).

In a theoretically complete dehalogenation of a polymer having initially 26.1% chlorine, there was obtained a product that had poorer agreement with the calculated composition. Calcd.: C, 58.7; H, 7.4. Found: C, 58.3; H, 6.31; Cl, 9.5.

The results of a large number of dehalogenation experiments are summarized in Table III. It should be pointed out that it is not entirely correct to obtain from Wall's formulas[9, 10] values for the calculated mole fraction of chlorine remaining in the case of polymers isolated after incomplete polymerization.

There were dozens of other similar experiments performed but these can be taken as illustrative. In some of these experiments polymer precipitated; in others it did not. In a few experiments the reactions were carried on for as long as thirteen days. In general, this made little difference in the results. The reaction does not seem to be sufficiently quantitative to be useful.

The polymer remaining after the zinc treatment of a "Vinylite" having a chlorine content of 43.7% was soluble in dioxane, did not decolorize a cold dilute potassium permanganate solution in acetone, but did decolorize a solution of bromine in carbon tetrachloride.

Solubility Experiments.—A mixture made up of 2.010 g. of polyvinyl acetate, 2.018 g. of polyvinyl chloride and 1.986 g. of a "Vinylite" containing 36.9% chlorine was extracted with 40 cc. of 1-heptyne. After filtering and evaporating the solution 1.589 g. of residue was obtained. This residue was purified by dissolving in dioxane and precipitating the polymer in water. The chlorine content was 1.49%. The residue from the first extraction was then treated with 25 cc. of phenylacetylene. This solution on evaporation gave 1.480 g. of polymer containing 18.7% chlorine. The material insoluble in the two acetylenes weighed 3.154 g. and contained 50.9% chlorine. The weight of the total recovered material is somewhat higher than that used, because the surplus amount of solvent is held by the polymer under the conditions of the experiment. This is lost in the purification of the product, but also a considerable amount of polymer is lost, and that introduces a still greater error into the figures.

This experiment was typical of several which showed that only a small amount of very low chlorine "Vinylite" would be found in the heptyne extract whereas "Vinylite" containing up to 65% vinyl chloride was soluble in phenylacetylene. By using these two solvents on samples of copolymers separation into fractions was obtained. Some of these separations are listed in Table IV.

The last two samples of copolymer reported in Table IV were prepared by the interrupted technique. The last one which was obtained by stopping polymerization at a 51% yield seems to be more homogeneous than the preceding sample which was made by stopping the polymerization after an 83% yield.

Hydrolysis of "Vinylite" to a Polychlorohydrin.—To a solution of 10 g. of "Vinylite" in 1 l. of dioxane was added 25 cc. of concentrated hydrochloric acid and 25 cc. of 95% ethyl alcohol. The mixture was heated to 50° for twelve hours and a deep red color developed. An additional 25 cc. of alcohol was added and the solution was boiled under a reflux condenser for eleven hours. The polymer was then precipitated by spraying the solution into water. A brownish polymer was obtained which was richer in chlorine than was the original. Two different copolymers were hydrolyzed by this procedure. The analytical figures before and after hydrolysis indicate conversion of the acetate groups to hydroxyl groups.

	Sample 1			Sample 2
	% C	% H	% Cl	% Cl
Anal. before hydrolysis	47.45	5.83	26.5	46.6
Anal. after hydrolysis	45.65	6.48	34.0	49.4
Calcd. for polychlorohydrin	44.4	6.42	35.8	51.1

The polychlorohydrin obtained in this manner did not show reduction of periodic acid solution. The chlorine atoms could not be hydrolyzed to hydroxyl by moist silver oxide or by treatment with mercuric acetate. The polychlorohydrin did not liberate iodine from an acetone solution of potassium iodide.

Contrary to the statements in the literature[22] we could not hydrolyze by means of aqueous alkali a copolymer of vinyl chloride and vinyl acetate prepared by exposing a methanol solution of the monomers and uranyl nitrate to sunlight.

Summary

1. Vinyl chloride and vinyl acetate copolymerize to produce polymer chains containing both units. However, the polymer molecules produced in a given case differ widely in composition and the first chains produced are richer in vinyl chlo-

(22) German Patents 362,666, 516,996.

ride than is the monomer mixture from which they are formed. The copolymers made by complete polymerization of a given starting mixture of monomer vary in composition from chain to chain.

2. The monomer units appear to be oriented in a 1,3-fashion in the polymer chain.

3. Some reactions of these copolymers have been described.

URBANA, ILLINOIS　　　　　　　　RECEIVED MAY 27, 1942

The Acid Catalyzed Hydrolysis of Phenyl Substituted Aliphatic Esters[1]

BY HILTON A. SMITH AND R. R. MYERS

In a recent publication[2] a study of the effect of the character of an alkyl chain on the reaction velocity of acid hydrolysis was reported for a number of esters of aliphatic acids. It was demonstrated that the effects were similar to those produced in the processes of esterification[3] and of saponification of the same (ethyl) esters.[4]

The purpose of the present paper is to report the results of a study of the velocity of hydrolysis of a number of phenyl substituted aliphatic esters, and to compare these results with those previously reported for saponification of the same esters[5] and for the acid-catalyzed esterification of phenylacetic, hydrocinnamic and γ-phenylbutyric acids in absolute methanol.[6]

Experimental

All of the esters were prepared by esterification of the corresponding organic acid with absolute ethanol using sulfuric acid as a catalyst. The esters were purified by fractionation in efficient distillation columns. Each sample used for rate measurements distilled at a constant head temperature and was also shown by analysis using the method already described[4] to be, within the precision of the method, 100% pure.

Phenylacetic, hydrocinnamic, phenylethylacetic and **diphenylacetic** acids were obtained from Eastman Kodak Co.; γ-phenylbutyric, δ-phenylvaleric, cyclohexylacetic and hydratropic acids were all prepared by methods which have been previously described.[5,6,7]

The hydrolyses were all carried out in 70%

acetone solution, the concentration of both ester and catalyst (hydrochloric acid) being 0.1 M. The acetone used in making up the medium was carefully purified by fractionation from alkaline permanganate in a five-foot, one-inch diameter column packed with glass helices. The fraction retained distilled at constant head temperature. The method employed in making up the reaction mixtures was the same as that already described by Smith and Steele,[2] and the general experimental procedure was also the same. Corrections were made for the contraction in volume which occurs when acetone is mixed with water and also for thermal expansion of the solvent. The reactions were run in electrically heated water thermostats which gave temperatures constant to ±0.01°.

Experimental Calculations and Results

The rate constants were calculated using the expression for a first order reaction

$$k = \frac{2.303 \log a/(a - x)}{(\text{catalyst})t}$$

where a is the initial ester concentration, x is the concentration of organic acid formed after time t, and the (catalyst) is the concentration of added

(1) Presented at the Memphis meeting of the American Chemical Society, April 22, 1942.

(2) Smith and Steele, THIS JOURNAL, 63, 3466 (1941).

(3) Smith, ibid., 62, 1136 (1940).

(4) Levenson and Smith, ibid., 62, 1556 (1940).

(5) Levenson and Smith, ibid., 62, 2324 (1940).

(6) Smith, ibid., 61, 1176 (1939).

(7) The authors are indebted to Mr. H. S. Levenson and Mr. J. H. Steele for the preparation and analysis of some of the esters used in this research.

TABLE I

ACID CATALYZED HYDROLYSIS OF ETHYL δ-PHENYLVALERATE IN 70% ACETONE AT 30°

a = (ester) = (HCl) = 0.100 M

t, minutes	$(a - x)$	$10^6 k$, liters moles^{-1} sec.$^{-1}$
5	0.0999	....
2080	.1246	22.6
2690	.1304	22.6
2980	.1331	22.5
3500	.1379	22.7
4240	.1429	22.0
4360	.1449	22.8
5025	.1497	22.9
5440	.1539	23.8
Average, 20–50%		22.6