stirring rod held against the side. The rubber stopper containing the air pressure line was plugged firmly into place and 60 cm. pressure was applied. The top of the tube had been calibrated at 10-ml. intervals starting from the top of the column and as the level of the liquid passed each mark, a new flask was put under the column, care being taken not to miss a drop in the transfer. When 10 ml. was left above the column, another 50 ml. of chloroform saturated with water was added and the pressure reapplied. In this manner 100 ml. of chloroform, 100 ml. of 5% *n*-butanol–95% chloroform V/V, 100 ml. of 10% *n*-butanol, and 100 ml. of 15% *n*-butanol were added.

To the 10-ml. fractions collected, one drop of phenol red indicator and one drop of Dreft solution were added and the solutions were titrated with 0.0203 *N* aqueous sodium hydroxide. The milliequivalents of acid in each fraction was calculated using a blank value of 0.01 ml. of base. A graph of milliliters of effluent *vs.* milliequivalents of acid was plotted and the points connected by a smooth curve (Fig. 2).

Determination of **Peak Effluent Volumes.**—The peak effluent volumes given in Table I were determined using the following known mixtures:

(1) Adipic (0.0845),[a] glutaric (0.0954), succinic (0.1154), malonic (0.1295), oxalic (0.1911).
(2) Mandelic[b] (0.0449), lactic (0.0978), glycolic (0.1008), malic (0.0929), citric (0.1422), tartaric (0.1640), glyceric (0.0355).
(3) β-Carboxyadipic (0.1557), tricarballylic (0.1092).
(4) *n*-Butyric[b] (0.0788), propionic[b] (0.1217), acetic[b] (0.1732), formic[b] (0.2590).
(5) Benzoic[b] (0.0594), phthalic (0.1156), trimesic (0.1440), gallic (0.0744), citric (0.1255).
(6) Chloroacetic (0.1197), trichloroacetic (0.0765), cyanoacetic (0.1028), itaconic (0.1451), citraconic (0.1014), aconitic (0.1201).
(7) Sebacic[b] (0.0835), suberic[b] (0.0731), adipic[b] (0.0120), glutaric[b] (0.2061).
(8) *m*-Hydroxybenzoic (0.0493), crotonic[b] (0.0712), *p*-hydroxybenzoic[c] (0.0652), fumaric (0.0677)[c], maleic (0.1121).
(9) Salicylic[b] (0.0478), chloroacetic[b] (0.0777), trimesic (0.1012), itaconic (0.1272).
(10) Benzoic[b] (0.1035), trichloroacetic[b] (0.1702), cyanoacetic[b] (0.0727).

[a] Milliequivalents, calculated from the weight and measured neutral equivalent. [b] Added to the column in chloroform solution after the others were added in alcohol–chloroform solution. [c] The peak effluent volumes of these acids were verified in other experiments not reported here.

Summary

A procedure for the separation of water-soluble organic acids using partition chromatography is described. This method is suitable for qualitative and quantitative determination of acids in mixtures.

The "peak effluent volumes" of thirty-six acids as determined by a standard procedure are listed. Mixtures containing acids of such closely related structures as *o*-, *m*- and *p*-hydroxybenzoic, lactic and glycolic, malic and tartaric, aconitic and tricarballylic, or adipic, glutaric, succinic, malonic and oxalic are easily separated. Sebacic and suberic or other acid mixtures that are not separated by the standard procedure may be separated by modification of it.

URBANA, ILLINOIS RECEIVED DECEMBER 16, 1949

[COMMUNICATION NO. 1274 FROM THE KODAK RESEARCH LABORATORIES]

The Structure of Ester-Lactone Polymers.[1] I. Ester-Lactones of the Maleic Anhydride–Vinyl Acetate Interpolymer

BY L. M. MINSK, G. P. WAUGH AND W. O. KENYON

Though maleic anhydride does not homopolymerize, it forms interpolymers with a variety of unsaturates.[2] The interpolymer with vinyl acetate consists of equimolar ratios of the two monomers in alternate array.[3] Upon treatment with alcohol and an acid catalyst, this interpolymer undergoes deacetylation, esterification and lactonization.[4] Resins of ester-lactone structures result from similar chemical treatment of the interpolymers of vinyl acetate with fumaric or maleic esters.

The structure assigned in the original disclosure of the ester-lactone resin[4] was based on certain chemical transformations and analyses of the product,[5] which involved determinations of the acetyl, free carboxyl and total saponification values. To confirm the compositions of these derived polymers, it was necessary to refine old and to devise additional analytical methods, particularly for those ester-lactones containing alkyl groups higher than ethyl.

The structures given may be assigned to the intermediate interpolymer and the derived ester-lactones.

Both γ- and δ-lactones are possible. The analytical methods here described do not discriminate between the two forms, since the analytical fragments are similar in both.

The anhydride interpolymer possesses acetyl and anhydride groups, and a small amount of free carboxyl, not indicated in the structural formula, which arises from slight hydrolysis. All three components should be determined in order that the summation of the analyses yield a complete description of the resin structure. The acetyl groups can be calculated to vinyl acetate, the anhydride groups to maleic anhydride, and the free carboxyl groups to maleic acid.

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(1) Presented before the High Polymer Forum of the American Chemical Society at the Atlantic City, N. J., meeting, September, 1949.

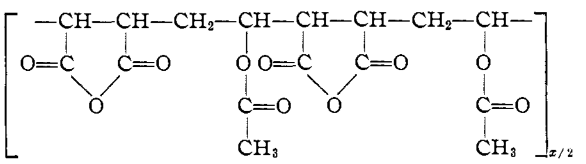
(2) Voss and Dickhauser, German Patent 540,101, November 26, 1931, to I. G. Farbenindustrie A.-G.

(3) Tong and Kenyon, THIS JOURNAL, **71**, 1925 (1949).

(4) McNally and Van Dyke, U. S. Patent 2,306,071, December 12, 1942, to Eastman Kodak Company.

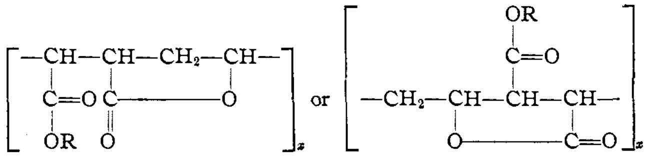
(5) Unpublished research of the late Dr. F. P. Pingert, formerly of these Laboratories.

A.

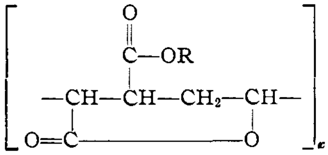


Maleic Anhydride–Vinyl Acetate Interpolymer

B.



γ-Ester–Lactone Derivative of A
(The two lactone formulas represent possible isomeric modifications)

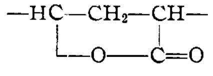


δ-Ester-Lactone Derivative of A

The ester-lactone contains essentially ester and lactone groups with varying amounts of free carboxyl and acetyl groups resulting from incomplete reaction. The amount of free hydroxyl groups is believed to be relatively small in the resins prepared in the usual manner.[4]

The analyses of the ester-lactone resin offers certain inherent difficulties. Calculated theoretical values depend upon assumptions concerning the composition of the resin. Analytically, the lactone and ester groups are similar in reaction. The maleic ester group of the methyl or ethyl ester-lactone can be determined by the Zeisel method. The lactone may be calculated as the difference between total saponification value and the sum of the saponification equivalent of the vinyl acetate, maleic ester and maleic acid contents. However, the Zeisel method is not satisfactory for the butyl ester-lactones. Thus, lactone and butyl maleate contents are left as unknowns. A method for determining lactone was therefore developed.

The only direct criteria of accuracy are: (1) the results should be duplicable, preferably by more than one method; (2) the total structures calculated from the analyses should substantially equal 100%; and (3) the contents of the various groups indicated should be compatible with the composition of the anhydride resin used in the preparation of the ester resin. To satisfy the second of these criteria, the amount of acetyl groups is calculated as vinyl acetate, the free carboxyl as maleic acid, the butyl ester group as butyl maleate, and the lactone group according to the structure



Though considerable attention is given to analytical methods, these are of secondary importance to the primary objective of confirming the polymer structures.

Experimental

(A) Analysis of the Butyl Ester-Lactone Resin

The following analyses were performed on a single batch of butyl ester-lactone polymer prepared according to Example 4 of U. S. Patent 2,306,071.[4]

(1) **Free Carboxyl Content.**—Since this resin is insoluble in water, it was dissolved in an organic medium and the free carboxyl titrated directly. After preliminary study, acetone was chosen as a dispersing agent. An appreciable quantity of water is necessary to produce a suitable end-point with phenolphthalein. In the absence of alkali, the water precipitated the resin.

A 1.0-g. sample was dissolved in 100 cc. of acetone. A few drops of phenolphthalein indicator, 5 to 10 drops of 0.5 *N* aqueous sodium hydroxide and 100 cc. of water were added, producing a clear solution. This was titrated with 0.5 *N* alkali and the free acid was calculated as maleic acid. Results were obtained by two different analysts using the same batch of resin:

	Analyst A		Analyst B
1	0.70 cc. *N* alkali	1	0.70 cc.
2	.71 cc.	2	.67 cc.
3	.74 cc.		
4	.72 cc.		
Av.	.72 cc.		.685 cc.
Maleic acid,	4.17%		3.97%

(2) **Total Saponification Value.**—Heating the ester-lactone resin with 0.5 *N* aqueous sodium hydroxide for twenty-four hours on a steam-bath, then titrating the excess alkali, was unsatisfactory, not because of incomplete hydrolysis, but because of the extreme breadth of the end-point. Phenolphthalein indicator produced a light pink color, evident over a long range of acid addition, and the final result was doubtful. The following procedure was developed:

To a 0.5-g. sample of ester-lactone dissolved in 50 cc. of pyridine at 56° was added 25 cc. of 0.5 *N* aqueous sodium hydroxide. Phase separation occurred. After hydrolysis at 56°, the sample was diluted with 75 cc. of distilled water to effect solution, and excess alkali was titrated with 0.5 *N* acid. A very sharp end-point was obtained. To determine the proper time of heating at 56°, the following series of samples was run:

Time, minutes	Apparent acetyl, Analyst A	Apparent acetyl, Analyst B
15		43.7
30	42.7	44.9
60	43.9	44.4
120	44.1	44.6
240	44.2	44.8
300		44.7
1440		45.85

Two hours at 56° is sufficient for complete hydrolysis. Extended heating appears undesirable.

(3) **Determination of True Acetyl.**—The method adopted is very similar to that used for the determination of acyl radicals in cellulose esters.

Fifty cc. of 0.5 *N* aqueous sodium hydroxide was added to a 0.5-g. sample of the ester lactone. The stoppered (wired) flask was heated on a steam-bath for twenty-four hours. The contents were transferred to a 500-cc. round-bottom, short-neck flask with a steam inlet and a large modified Kjeldahl trap leading to a water-cooled coil or bulb condenser. The sample, acidified with 10 cc. of 2:1 (by volume) solution of water and 85% phosphoric acid, was steam-distilled, keeping the distilling volume at about 75–100 cc. When 2 to 2.5 liters of water distilled, the distillate was refluxed to remove carbon dioxide, cooled under a soda-lime tube and titrated with 0.5 *N* aqueous sodium hydroxide, using phenolphthalein indicator. Using this method of analysis, values of 6.47 and 6.56% of vinyl acetate were obtained.

(4) **Determination of Lactone.**—Selective hydrolysis was not successful since the ester groups were also attacked.

A method was devised which operated on the following principles: The lactone ester before hydrolysis contains butyl ester, lactone, acetyl and free carboxyl groups. By hydrolysis in alkali, the butyl ester unit yields the sodium resin salt and butyl alcohol, the lactone unit becomes a sodium resin salt and resin alcohol, the vinyl acetate unit gives resin alcohol and sodium acetate, and the free carboxyl unit becomes sodium resin salt. Excess hydrochloric acid should re-form the lactone. The solution will then contain: titratable polymer carboxyl from both the original ester and the free carboxyl units, acetic acid from the sodium acetate, excess hydrochloric acid, sodium chloride and the re-formed lactone. Every molecule of hydrochloric acid consumed liberates titratable carboxyl, either in the resin molecule or as free acetic acid. If no lactone were formed, the amount of alkali required for neutralization would be equivalent to the hydrochloric acid added. When the lactone is re-formed, titratable carboxyl is removed and the back-titration will be less than the theoretical by an amount equivalent to the amount of lactone formed. The decrease of titratable acidity is the lactone originally present, provided the lactone re-forms completely and no component, present before or formed during hydrolysis, now enters into lactone formation under the conditions of the analysis. The presence of substantial amounts of free hydroxyl groups in the ester resin as prepared has not been demonstrated, and an examination of the complete analyses of several butyl ester resins leads to the belief that the hydroxyl groups arising from hydrolysis of the residual vinyl acetate or carboxyl groups arising from the ester hydrolysis do not substantially interfere with the lactone determination.

The procedure is as follows: a 0.5-g. sample of resin was hydrolyzed according to the pyridine method of section A, 2 and the excess alkali titrated to the phenolphthalein endpoint. Twenty-five cc. of 0.5 *N* aqueous hydrochloric acid was added. The stopper was wired in the flask and the sample was maintained at about 75°. After cooling, excess hydrochloric acid was titrated. The difference between the acid added and the observed back-titration measures the lactone present. The accompanying table indicates that four hours produces complete lactone formation. The lactone was calculated from the formula given earlier in this paper (mol. wt. 84).

Heating, hr.	1	2	3	4	5	22
Lactone, %	30.9	32.1	32.5	32.3	32.2	31.3

Marked discoloration from very light yellow to deep brown occurred with prolonged heating.

The analytical values thus obtained for the lactone, carboxyl, and true acetyl contents of the ester lactone are summarized in Table I. The butyl maleate content was calculated from the apparent acetyl content and compared to that obtained by difference from 100%.

From these analyses, the calculated molar ratio of maleic anhydride to vinyl acetate in the original anhydride resin was 1.02/1. The value of 1.02/1, agrees with the resin structure (3) independently observed and with direct analyses of a number of such samples. If the lactone analysis is believed in error due to additional lactonization of hydroxyl or carboxyl groups arising from the saponification treatment of the *n*-butyl ester resin, a correction may be applied. Thus, on correcting the figures given above for hydroxyl, a lactone content of 26.2% and a *n*-butyl maleate content of 64.4% are obtained corresponding to a maleic anhydride–vinyl acetate ratio of 1.22/1. This disagrees with the analysis of the anhydride resin given below and shows that such correction is not warranted.

TABLE I

PER CENT. OF *n*-BUTYL MALEATE IN BUTYL ESTER-LACTONE CALCULATED FROM WEIGHT PER CENT.

Maleic acid	4.2% by weight
Lactone	32.5% by weight
Vinyl acetate	6.5% by weight
	43.2%

By difference the *n*-butyl maleate = 100 − 43.2% = 56.8%

Calculated from Titration Values

Total saponifiable	44.2%		10.25 cc.	1 *N* reagent/g.
Maleic acid	4.2%	0.72 cc.		
Vinyl acetate	6.5%	0.76 cc.		
Lactone	32.5%	3.88 cc.	5.36 cc.	1 *N* reagent/g.
	43.2%	5.36 cc.	4.89 cc.	1 *N* reagent/g.

4.89 cc. 1 *N* reagent/g., 55.8% *n*-butyl maleate

(B) The Analysis of the Maleic Anhydride–Vinyl Acetate Interpolymer

(1) **Anhydride and Free Carboxyl.**—This procedure consists in: (1) the determination of the carboxyl groups present after reaction of the resin with aniline, and (2) determination of the total carboxyl groups present after hydrolysis.

One gram of anhydride polymer was dissolved in 25 cc. of acetone. Freshly distilled, dry aniline (25 cc.) was added with shaking. After two hours at room temperature, 100 cc. of a 1:1 (vol.) water/95% ethanol was added and the free carboxyl was titrated with standard sodium hydroxide using phenolphthalein.

One carboxyl group should be present after aniline reaction for each original anhydride group. If no free carboxyl was present, the carboxyl value after aniline reaction should be exactly one-half of the total carboxyl as determined in B-2. If it is more than one-half, the difference is a measure of free carboxyl.

(2) **The Analysis of the Total Carboxyl.**—Titration after alkaline hydrolysis of the anhydride polymer gave the same broad titration end-point as with the butyl ester-lactone. Also, there was no assurance that the alkali treatment did not cause hydrolysis of acetyl groups.

Hydrolysis of anhydride groups in the absence of alkali was adopted. Preliminary experiments indicated opening of the anhydride ring, but alkali titrations gave uncertain end-points. The addition of pyridine remarkably sharpened the end-point. For a given weight of sample in a fixed volume of water, an increasing amount of alkali was required as more pyridine was added. Pyridine–water ratios greater than 1:1 (vol.) caused no further change in end-point. This end-point was assumed to be the true one.

The time of heating for complete hydrolysis of the anhydride was determined by the following series: one-gram samples of the vinyl acetate–maleic anhydride resin in 50 cc. of distilled water were heated on steam-baths for various periods, cooled, diluted with 50 cc. of pyridine and titrated with 0.4964 *N* aqueous sodium hydroxide, using phenolphthalein indicator. A heating period of two hours was adopted.

Time, hr.	1	2	4	6
Titrn., cc. alkali	21.62	21.68	21.73	21.62

(3) **True Acetyl.**—The true acetyl of the anhydride polymer was determined by a procedure similar to that described for the butyl ester-lactone and gave concordant results.

The results of a complete analysis of a sample of the anhydride interpolymer by the methods described above are

	Analyst A	Analyst B
Vinyl acetate	44.35	44.5
Maleic anhydride	44.25	45.25
Maleic acid	11.33	10.95
	99.93%	100.70% (wt.)

TABLE II

THE COMPOSITION OF BUTYL ESTER-LACTONES PREPARED USING VARIOUS AMOUNTS OF WATER

Moles water/mole anhydride unit		0	0.05	0.10	0.25	0.50	1.00	2.00	4.00	8.00
Maleic acid units	% by wt.	4.2	4.4	3.8	4.1	4.6	5.2	7.3	8.6	11.5
	Mole fraction	0.0495	0.0524	0.0446	0.0482	0.054	0.0607	0.0334	0.0966	0.126
Lactone units	% by wt.	28.8	29.1	29.5	29.6	29.7	30.8	32.0	34.9	36.7
	Mole fraction	0.468	0.472	0.477	0.482	0.482	0.497	0.504	0.542	0.557
Vinyl acetate units	% by wt.	8.9	8.9	7.9	7.7	7.4	6.3	7.0	4.6	3.2
	Mole fraction	0.141	0.141	0.125	0.122	0.117	0.0994	0.107	0.0698	0.0474
Butyl maleate units	% by wt.[a]	58.1	57.6	58.8	58.6	58.3	57.7	53.7	51.9	48.6
	% by wt.[b]	57.0	56.2	58.1	57.9	58.0	57.8	52.8	51.3	48.5
	Mole fraction[b]	0.342	0.335	0.353	0.347	0.347	0.343	0.305	0.293	0.272
Total saponification value	Cc. N alkali per gram of resin	10.20	10.20	10.20	10.22	10.28	10.37	10.50	10.67	10.98
Maleic/vinyl units ratio[c]		1.02	1.01	1.05	1.05	1.07	1.09	1.05	1.08	1.12
Total of analytical values[d]		98.9	98.6	99.3	99.3	99.7	100.1	99.1	99.4	99.9

[a] Calculated by weight difference using analytical values of vinyl acetate, lactone and maleic acid. [b] Calculated from total saponification value. [c] Calculated using maleic ester units from saponification values [b]. [d] Sum of maleic acid, lactone, vinyl acetate and determined butyl maleate units as weight per cent.

TABLE III

RECAPITULATION OF ANALYSES

	Ethyl ester-lactone			Isopropyl ester-lactone		
	% wt.	N alk./g.	N alk./g.	% wt.	N alk./g.	N alk./g.
Total saponifiable			11.61 cc.			11.68 cc.
Maleic acid units	8.4	1.44 cc.		20.9	3.60 cc.	
Vinyl acetate units	10.8	1.26 cc.		1.1	0.13 cc.	
Ethyl maleate units	44.5	5.18 cc.	7.88 cc.	33.2	3.32 cc.	7.05 cc.
	63.7	7.88 cc.	3.73 cc.	55.2	7.05 cc.	4.63 cc.
Lactone: From total saponifiable			31.3%		39.4%	
Lactone: From direct lactone analysis			30.9%		42.3%	
Maleic/vinyl ratio (lactone analysis)			1.04		1.06	

Discussion

The concordance of the methods and the structure of both the anhydride interpolymer and derived ester-lactone resin are attested by the analytical results. The ester-lactone analyses indicate an original maleic anhydride (acid)/vinyl acetate ratio of 1:02/1. The interpolymer used to prepare the lactone ester gave a ratio (B-3) of 1.06:1.

Table II summarizes the composition of a series of the *n*-butyl ester-lactone resins prepared in the presence of various amounts of water. As expected, the free carboxyl and lactone increase with increasing water content while vinyl acetate and *n*-butyl maleate groups decrease. This series was prepared from an interpolymer containing 51.1% of maleic anhydride units, 2.2% of maleic acid units and 45.4% of vinyl acetate units corresponding to a maleyl:vinyl ratio of 1.03:1. The ester-lactone resins prepared in the presence of large amounts of water were expected to have larger combined vinyl alcohol contents. However, the total analytical values substantially total 100%. There is an apparent increase in maleic:vinyl unit ratio with increasing water in the reaction mixture. Possibly the lactone analysis exceeds the true value as the content of combined acid in the lactone ester increases. More relactonization may occur than was originally present. This drift cannot be analytically serious because the shift in molar ratio of maleic anhydride to vinyl acetate, while present, is still small. It does, however, indicate that some combined polyvinyl alcohol is present which increases with the increasing amounts of water in the lactonization mixture.

Comparative data on typical ethyl and isopropyl ester-lactones are given in Table III. In these, the alkoxyl groups were determined by the Zeisel method[6] and calculated to the corresponding maleic ester contents.

In calculating the maleic:vinyl ratio of the ester lactone polymers, it should be borne in mind that each lactone unit is built from one half of a maleic anhydride unit for each vinyl acetate unit.

Summary

1 The published structures of the ester-lactone polymers are corroborated by analytical determination of various structural units.

2. The polymers include principally lactone and maleic ester units with small amounts of maleic acid, vinyl acetate and possibly vinyl alcohol units. The last were not directly determined.

3. From the analytical values, the ratios of maleic units to vinyl units in the ester-lactones were calculated as being essentially unity, which

[6] Analyses for alkoxyl supplied through the courtesy of the Cellulose Acetate Development Department of the Eastman Kodak Company.

is in agreement with the determined structure of the maleic anhydride–vinyl acetate resins used for esterification.

4. The analytical methods employed are described.

ROCHESTER, NEW YORK RECEIVED JULY 16, 1949

[COMMUNICATION NO. 1275 FROM THE KODAK RESEARCH LABORATORIES]

The Structure of Ester-Lactone Polymers.[1] II. Ester-Lactones of Poly-α-chloroacrylic Acid

BY L. M. MINSK AND W. O. KENYON

The tendency for poly-α-chloroacrylic acid to form a lactone is mentioned by Marvel and co-workers. These investigators found that when a solution of the polymer was boiled, a gel formed which filled the vessel and which, upon drying, gave a halogen-free, water-insoluble, powdery product. The authors believed this product to be a cross-linked lactone with some hydroxyl groups. Analytically, it is impossible to determine whether the reaction was principally intramolecular lactone formation or intermolecular esterification. From the insolubility of the product, it can only be concluded that reaction had occurred intermolecularly. The insoluble polymer probably contains lactone, intermolecular ester, hydroxyl and carboxyl groups.

The formation of intramolecular lactone along a polymeric chain was first observed by McNally and VanDyke.[3] Marvel and co-workers[2] mention the possibility of some lactone formation during the polymerization of the esters of α-chloroacrylic acid to explain the low halogen content of their products. Lactone formation has also been observed when certain copolymers of vinyl acetate and methyl acrylate are subjected to de-esterification in alcohol solution by acid catalysts.[4] In these cases, soluble products were obtained, definitely indicating intramolecular lactone formation.

The initial experiments reported herein employed a copolymer of α-chloroacrylic acid and vinyl acetate in an attempt to duplicate the lactonization behavior of the vinyl acetate–methyl acrylate copolymer,[4] while avoiding the cross-linking described by Marvel.[2] It soon became quite obvious from the experimental data that the vinyl acetate played little or no role in the lactonization and that, under suitable conditions, a soluble ester-lactone of the poly-α-chloroacrylic acid homopolymer could be obtained. The emphasis was therefore shifted to the homopolymer. Much of the experimental has been disclosed in patents and need not be reiterated.[5] Rather, this paper presents the chemical and analytical data which support the intramolecular lactone resin structure.

Experimental

α-Chloroacrylic acid was prepared by the following improvement of the method of Crawford and McLeish.[6] The condensation was run as described in Example 3 but quantities were increased ninefold and 5 g. of copper sulfate were added to inhibit polymerization. The condensation mixture and 900 cc. of distilled water were placed in a modified Claisen flask connected through a wide bore condenser to a 5-liter, three-neck flask, chilled in an ice and salt-bath. Copper sulfate was placed in the receiver to prevent polymerization. Distillation at atmospheric pressure for approximately thirty minutes gave 700 to 900 cc. of distillate. This distillate was removed, the copper sulfate was replenished, and a vacuum was applied slowly to the receiver through a short condenser as the distilland cooled until approximately 20 mm. pressure was reached. Distillation was continued at this pressure and water was admitted below the level of the distilland, at a rate equal to distillation. The distilling vapors were chilled quickly and kept cold after condensation. The short, unpacked, distillation column and condenser were wide bore to prevent clogging due to crystallization of α-chloroacrylic acid. It was thus possible to obtain the α-chloroacrylic acid in a total of 2 to 3 liters of distillate and to extract it therefrom with three one-liter portions of ether. The ether extract was dried over calcium chloride in an ice chest, the ether was completely removed under vacuum at as low a temperature as possible, and the crude α-chloroacrylic acid was recrystallized once from Skellysolve G (petroleum hydrocarbon, b. p. 50–70°). The yields were of the order of 450 g.

Polymerization of α-chloroacrylic acid of this purity yielded products whose molecular weight varied with different batches of monomer. All acid was therefore recrystallized using 700 g. of acid, 2300 cc. of Skellysolve G, and 10 g. of decolorizing carbon. The recovery was of the order of 600 g. of snow-white crystals, m. p. 66.5 to 67°.

Copolymerization of α-Chloroacrylic Acid and Vinyl Acetate.—Fifty-three and a half grams of α-chloroacrylic acid, 43.0 g. of vinyl acetate, and 0.0965 g. of benzoyl peroxide were polymerized for twenty-two hours at 50°, protected from moisture by a calcium chloride tube. The solid white polymer was dissolved in 300 cc. of 9:1 by volume acetone–water mixture, precipitated in ether, washed with ether and vacuum-dried. Excessive drying caused darkening. The product contained 71.5% combined chloroacrylic acid and 12.8% vinyl acetate units as calculated from chlorine and acetyl analyses. The 15.7% unaccounted for may be spontaneously formed lactone or retained ether.

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[1] Presented before the High Polymer Forum of the American Chemical Society at the Atlantic City, New Jersey, meeting, September, 1949.

[2] Marvel, Dec, Carter and Cowan, THIS JOURNAL, **62**, 3498 (1940).

[3] U. S. Patent 2,306,071, December 22, 1942, to Eastman Kodak Company; see also ref. 11.

[4] Kenyon, Murray and Minsk, U. S. Patent 2,403,004, July 2, 1946, to Eastman Kodak Company.

[5] Kenyon and Minsk, U. S. Patent 2,413,716, January 7, 1947, to Eastman Kodak Company; see also British Patent 561,337; French Patent 946,236; Canadian Patent 456,874.

[6] U. S. Patent 2,233,835, March 4, 1941 to Imperial Chemical Industries Ltd. (see specifically Example 3).