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

4. The analytical methods employed are described.

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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 coworkers. 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 deesterification 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).

Homopolymerization of α-Chloroacrylic Acid.—One part of α-chloroacrylic acid, 2 parts of dry 1,4-dioxane, and 0.003 part of benzoyl peroxide were polymerized at 100° for three hours. A clear, viscous dope was obtained. The polymer was isolated (when necessary) by dilution with dry dioxane and precipitation in ether and then treated as described for the copolymer. An analytical sample dried for three days *in vacuo* over calcium chloride contained 22.04% chlorine (theory, 33.3).

From the standpoint of structure, molecular weight is of minor importance. Optimum physical properties were obtained only at high molecular weight. The polymerization of α-chloroacrylic acid responded normally to temperature and catalyst concentration. Optimum yields were obtained when at least 0.3% of benzoyl peroxide, based on monomer, was used. For highest molecular weight, an inert atmosphere was used.

Lactonization and Esterification.—Early work was done with isolated polymer. Later it was found, particularly with the homopolymer where polymerization is quantitative, that isolation was not necessary and that lactonization, with esterification, results by treatment of the 1,4-dioxane polymerization dope with a primary alcohol. The isolated primary polymer requires water to effect solution in alcohols. Sulfuric acid catalyst was used initially but was later found unnecessary.

Complete analyses can be obtained only on the methyl, ethyl and possibly the isopropyl esters. Alkoxyl determinations cannot be accurately made for higher groups. The ethyl ester-lactones are described in detail.

Ethyl Ester-Lactone of the α-Chloroacrylic Acid-Vinyl Acetate Copolymer.—Ten grams of vinyl acetate-α-chloroacrylic acid polymer was dissolved in 90 cc. of 10:1 (volume) absolute ethyl alcohol-water solution in an all-glass reflux outfit on a steam-bath. Two cc. of concentrated sulfuric acid in 10 cc. of 10:1 ethyl alcohol and water were added. After seven and one-half hours the product separated as a cake. The polymer was dispersed in 100 cc. of acetone and precipitated in distilled water. Reprecipitation in distilled water, washing until acid-free, and drying, yielded 6.4 g. of white fibrous product, soluble in acetone. *Anal.* Cl, 8.64; ethoxyl, 13.7; acetyl, 5.8; total saponifiable, 13.46 cc. *N* alkali/g.; titratable acidity, 1.16 cc. *N* alkali/g.

Ester-Lactones of Poly-α-chloroacrylic Acid Homopolymer.—The procedure was similar to the above using 100 g. of homopolymer in 400 cc. of 10:1 (volume) alcohol-water mixture, and 5 cc. of concentrated sulfuric acid in 150 cc. of 10:1 alcohol-water mixture. Lactonization proceeded for four hours. The resin cake was purified as previously described. The results are given in Table I.

TABLE I

ESTER-LACTONES OF POLY-α-CHLOROACRYLIC ACID

Expt.	Alcohol	Yield, g.	η sp	Total saponifiable[a]	Alkoxyl, %	Chlorine, %	Carboxyl[a]
1	Methyl	46	[b]	[b]	8.2	8.19	3.26
2	Ethyl	52	0.056	13.32	16.7	8.35	1.22
3	*n*-Propyl	57	.065	...	..	7.38	0.48
4	*n*-Butyl	59	.070	...	..	7.55	.55
5	*n*-Butyl[c]	57	...	12.15	..	7.3	.57

[a] Cc. *N* alkali/g. [b] Not completely soluble. [c] Made without isolation of the intermediate homopolymer. No sulfuric acid catalyst.

Effect of Liquid/Solid Ratio on the Lactonization of Poly-α-chloroacrylic Acid.—Three 100-g. samples of α-chloroacrylic acid were polymerized at 50° in 200 cc. of dry 1,4-dioxane with 0.300 g. of benzoyl peroxide. To each were added the indicated amounts of 10:1 (volume) *n*-butyl alcohol-water mixtures, previously warmed to 70°. After lactonization for twenty-four hours on a steam-bath, the dopes, diluted with acetone, were precipitated in distilled water. The products were reprecipitated from acetone into distilled water until they were obtained in fibrous form, washed free of acid, and dried at 60°. The results in Table II indicate that the amount of lactonizing alcohol must exceed a certain minimum.

TABLE II

EFFECT OF LIQUID-SOLID RATIO ON LACTONIZATION

Expt.	*n*-Butyl alcohol-water added, cc.	Yield, g.	η sp	Carboxyl cc. *N* alkali/g.	Chlorine, %
1	100	Gelled during lactonization step			
2	200	74	0.080	0.76	9.53
3	300	90	.070	.62	9.63

Below this, the probability of a carboxyl reacting with a chlorine (or hydroxyl) on an adjacent chain is high and sufficient intermolecular esterification occurs to insolubilize the product.

The Effect of Water upon the Lactonization of Poly-α-chloroacrylic Acid.—One-hundred-gram samples of α-chloroacrylic acid were polymerized in dioxane as previously described and to each was added 175 cc. of the indicated *n*-butyl alcohol-water mixture. Lactonization and isolation were as described. The results are given in Table III.

TABLE III

EFFECT OF WATER UPON THE LACTONIZATION OF POLY-α-CHLOROACRYLIC ACID

Expt.	*n*-Butyl alcohol-water ratio (by volume)	Yield, g.	Carboxyl, cc. *N*/g.	Chlorine, %	Lactone, cc. *N*/g.	η sp
1	10:0	100	0.18[a]	11.03	3.52[a]	0.052
2	10:1	93	.45[a] .40[b]	8.96	...	.033
3	10:2	84	.90[a] 1.04[b]	6.69	5.36	.032
4	10:3	83	1.29[a] 1.60[b]	7.44		.038
5	10:4	Gelled				

[a] Determined by titration using phenol red end-point.
[b] Determined by electrometric titration.

Increasing amounts of water increase carboxyl and lactone contents. When sufficient water is present, insolubilization through cross-linking occurs. The yield decreases since lactone is formed at the expense of simple ester.

The Effect of Heating Time on Lactonization.—Two hundred grams of α-chloroacrylic acid was polymerized in dioxane in the usual way and lactonized on a steam-bath by the addition of 700 cc. of 10:1 *n*-butyl alcohol-water mixture. Samples were removed at intervals, diluted with acetone and worked up in the usual way. The results are given in Table IV.

TABLE IV

EFFECT OF HEATING TIME ON THE LACTONIZATION OF POLY-α-CHLOROACRYLIC ACID

Expt.	Heating time, in hours	Carboxyl, cc. *N* alkali/g.	Chlorine, %	η sp
1	1	Water-soluble		
2	2	Water-soluble		
3	2.5	Sample pptd. by water. Too gelatinous to handle		
4	4	Sample pptd. by water. Gelled in acetone during purification		
5	6	1.21	6.57	0.097
6	8	0.92	9.20	.094

Analytical

Specific Viscosity.—The flow time in an Ostwald viscometer of a solution of 0.100 g. of polymer dissolved in acetone to make 100 cc. of solution was determined at 25°. The specific viscosity (η sp) is the flow time of the solution divided by the flow time of the solvent, minus one.

Chlorine.—Chlorine was determined by the micro-Dumas method.[7]

Alkoxyl.—Alkoxyl was determined by the Zeisel method.[8]

Acetyl.—Acetyl was determined by the standard distillation method, corrected by a chloride analysis upon the distillate.[8]

Carboxyl.—Two-tenths gram of sample was dispersed in 20 cc. of acetone, diluted by 80 cc. of distilled water and titrated rapidly with 0.1 *N* sodium hydroxide, with phenol red as the internal indicator. The first appearance of red was taken as the end-point, since it is fleeting, probably due to the hydrolysis of halogen and lactone. The titration may also be followed electrometrically (Table III).

Total Saponifiable.—The procedure was similar to that used for analysis of polyvinyl acetate,[9] except that three hours were required for complete saponification and the end-point at *p*H 8.3 was read electrometrically because of the darkening of the solution during saponification.

Lactone.—The presence of lactone is difficult to demonstrate directly through fission and isolation of fragments. Upon opening, the fission products remain attached to the polymer chain, though acidity is developed. Its presence, therefore, can only be deduced from the chemical behavior of the polymer. There are several indirect methods by which the presence of lactone can be demonstrated and estimated. (A) In the case of ester-lactones of poly-α-chloroacrylic acid, the known alkali-consuming components are ester, chloride, carboxyl, acetyl (in the copolymer with vinyl acetate) and lastly, lactone. In the ethyl ester-lactone all except the last may be separately estimated. The difference between these and total saponification value must be due to lactone. This treatment was given to the two ethyl ester-lactones, reducing all analytical data to terms of cc. of *N* sodium hydroxide per gram. (1) The ethyl ester-lactone of the α-chloroacrylate-vinyl acetate copolymer. Total saponifiable acidity equivalent to 13.46 cc.

Accountable acidity

Chlorine (8.65%) = 2.44 cc. *N*/g.
Ethoxyl (13.7%) = 3.05
Acetyl (5.8%) = 1.35
Carboxyl = 1.16
Total 8.00

Lactone by difference, 13.46 − 8.00 = 5.46 cc. *N*/g.

(2) Ethyl ester-lactone of poly-α-chloroacrylic acid. Total saponifiable acidity, 13.32 cc.

Chlorine (8.35%) = 2.35
Ethoxyl (16.7%) = 3.71
Carboxyl = 1.22
Total 7.28

Lactone by difference, 13.32 − 7.28 = 6.04 cc.

(B) The lactone ring may be opened through controlled saponification.[10] To the sample, after determination of free carboxyl, was added 20 cc. of 0.1 *N* sodium hydroxide. After one hour at room temperature, excess alkali was titrated back to the phenol red end-point. The titration value as obtained, corrected for the chlorine content of the polymer, yielded lactone estimates (in terms of cc. *N* alkali/g.) in fair agreement with the value found by method A above, for the ester lactones of the copolymer and homopolymer of α-chloroacrylic acid.

	Copolymer, cc.	Homopolymer, cc.
Alkali consumed	8.63	8.92
Chlorine	2.44	2.35
Estimated lactone	6.19	6.67
Lactone previously found by difference	5.46	6.04

The values thus obtained are higher than those from total saponification but of the same order of magnitude. For those ester-lactones whose alkoxyl groups cannot be directly estimated, these values may serve as a first approximation for the determination of the ester by difference, again from complete saponification data. Whenever possible, the lactone value obtained from the total saponification data is preferable.

(C) Lactone groups may be demonstrated and estimated in the ester lactones derived from the vinyl acetate–maleic anhydride interpolymer by a relactonization after complete saponification.[11] This procedure, applied to the ethyl and butyl ester-lactones of the α-chloroacrylic acid homopolymer, gave low lactone values equivalent to 3.12 and 2.13 cc. *N* reagent/g. While these values may demonstrate the presence of lactone, they do not appear to be valid estimates.

Samples whose lactones had been opened by alkali in method B, were relactonized by the addition of 20.0 cc. 0.1 *N* and heating for 1.5 to 2 hours. Titration showed a loss in acid value, *i. e.*, a relactonization value equivalent to 4.05 and 5.53 cc. for the ethyl ester-lactones of the homo- and copolymer, respectively. The value for the homopolymer is lower than those found by the other two methods but not unexpectedly so, since the acid treatment would tend to generate carboxyl through hydrolysis of ester. This method does not appear to be reliable, but again demonstrates the re-formation of lactone by acid treatment.

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(7) We are indebted to the Microanalytical Section of these Laboratories for these analyses.

(8) We are indebted to the Cellulose Acetate Development Department of Eastman Kodak Co., for these analyses.

(9) Minsk, Priest and Kenyon, This Journal, **63**, 2716 (1941).

(10) Suggested by Dr. J. Russell of these Laboratories.

(11) Minsk, Waugh and Kenyon, This Journal, **72**, 2646 (1950).

TABLE V

SUMMATIONS FOR HYDROXYL

Ester-Lactone of the α-Chloroacrylic Acid-Vinyl Acetate Copolymer

Carboxyl	1.16	Chlorine	2.44
Ethoxyl	3.05	Lactone	5.46
Lactone	5.46	Total	7.90
Total	9.67		

Hydroxyl ~1.77 cc. = 3.01%

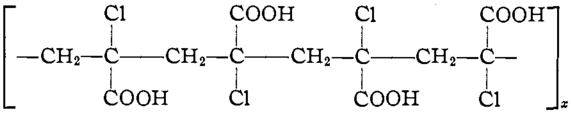
Ester-Lactone of the α-Chloroacrylic Homopolymer

Carboxyl	1.22	Chlorine	2.35
Ethoxyl	3.71	Lactone	6.04
Lactone	6.04	Total	8.39
Total	10.97		

Hydroxyl ~2.58 cc. = 4.39%

Hydroxyl.—The last component that may be present in the molecule of the ester-lactone is hydroxyl, or unsaturation due to dehydrohalogenation. The latter is unlikely and will be neglected. The usual methods for determination of hydroxyl are of doubtful applicability to the present polymer. The problem may be approached indirectly. Poly-α-chloroacrylic acid contains halogen and carboxyl in equimolar ratios. This ratio must persist in any derivative, though the form may change. Carboxyl may become ester, lactone, or remain as such, while chlorine may become lactone, hydroxyl, or remain unchanged. Therefore, the molar total of chlorine, lactone and hydroxyl must equal the molar total of lactone, ester and carboxyl. The deviation of the former analyzable totals from the latter must be hydroxyl. The summations in terms of cc. of N reagent are given above in Table V. In the copolymer we have neglected the acetyl since this remains essentially unchanged.

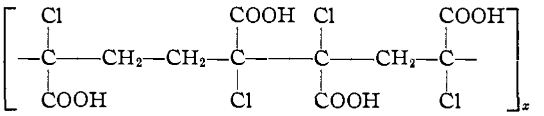
The Structure of the α-Chloroacrylic Acid Ester-Lactones.—The only criterion available for the correctness of a series of analyses of this type is to assign a structure to the product and to reconcile that structure with the analytical data. From these data it is not possible to assign either a head-to-head, or head-to-tail structure to the α-chloroacrylic acid polymers though Marvel and Cowan[12] have assigned a head-to-head structure to the esters. Analogy fails here, for, though poly-α-chloroacrylic acid lactonizes readily, the esters do not. At this time it appears preferable to treat the matter of structure of the intermediate as an open problem. If polymerization is head-to-tail, then poly-α-chloroacrylic acid has the structure (1)



$$\left[-CH_2-\overset{Cl}{\underset{COOH}{C}}-CH_2-\overset{COOH}{\underset{Cl}{C}}-CH_2-\overset{Cl}{\underset{COOH}{C}}-CH_2-\overset{COOH}{\underset{Cl}{C}}-\right]_x$$

(1)

If head to head, this structure (2)

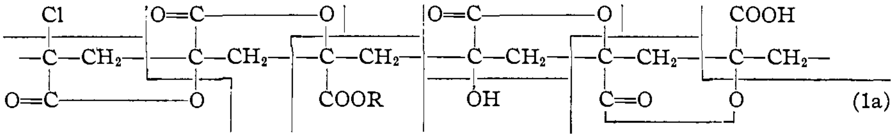


$$\left[-\overset{Cl}{\underset{COOH}{C}}-CH_2-CH_2-\overset{COOH}{\underset{Cl}{C}}-\overset{Cl}{\underset{COOH}{C}}-CH_2-\overset{COOH}{\underset{Cl}{C}}-\right]_x$$

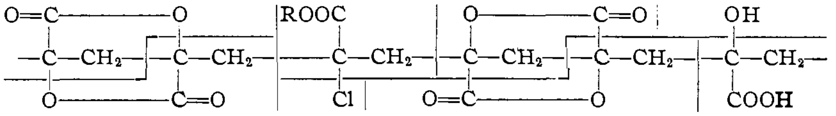
(2)

From the standpoint of lactonization, it is immaterial, since both γ- and δ-lactones form with great ease.

Upon lactonization, structure (1) may yield one of two forms (1a or 1b) or a mixture of both, since the carboxyl may swing in either direction to a γ-chlorine.

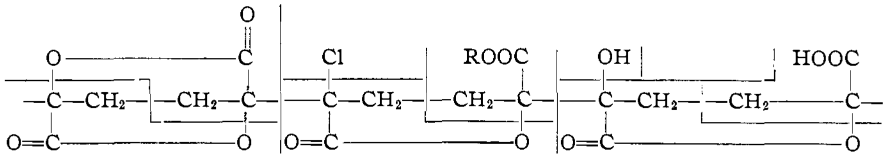


(1a)



(1b)

If the intermediate has a head-to-head structure, then only one form for the lactone is possible, for the carboxyl can swing only in one direction to a δ-halogen. In the other direction, the halogen is β, and not readily lactonizable.



(2a)

The diagrams are purely illustrative, with no attempt to adhere to analytical proportions. Analytically, the net result is independent of the geometry of the intermediate. All three lactone structures may be calculated in terms of indicated units common to each. By converting the analytical data into weight percentages of these units (Table VI), the sum should be 100%, within the limits of analytical accuracy (Table VII).

Discussion

The experimental evidence confirms the tendency for poly-α-chloroacrylic acid to lactonize.[2] The isolated polymer, though it contains con-

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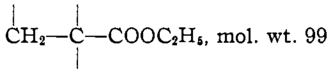
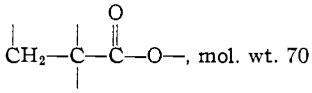
(12) Marvel and Cowan, THIS JOURNAL, 61, 3156 (1939).

TABLE VI

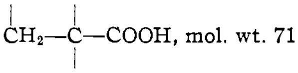
STRUCTURAL FRAGMENTS

Chlorine was calculated as Cl, mol. wt. 35.5

Ethoxyl as  $-CH_2-C(-)(-)-COOC_2H_5$, mol. wt. 99

Lactone as  $-CH_2-C(-)(-)-C(=O)-O-$, mol. wt. 70

Hydroxyl as —OH, mol. wt. 17

Carboxyl as  $-CH_2-C(-)(-)-COOH$, mol. wt. 71

Acetyl as  $-CH_2-CH(-)-OCOCH_3-$, mol. wt. 86

TABLE VII

SUMMATION OF STRUCTURAL FRAGMENTS OF ETHYL ESTER-LACTONES

Analytical fragment	Chloroacrylic acid-vinyl acetate copolymer Found	Weight % structural fragment	α-Chloroacrylic homopolymer Found	Weight % structural fragment
Hydroxyl	3.01%	3.01	4.48%	4.48
Chlorine	8.65%	8.65	8.19%	8.19
Ethoxyl	13.7%	30.30	16.7%	36.70
Acetyl	5.8%	10.60		
Carboxyl	≈1.16 cc. *N*/g.	8.24	1.20 cc. *N*/g.	8.56
Lactone[a]	≈5.46 cc. *N*/g.	38.22	6.04 cc. *N*/g.	42.28
	Total	99.02	Total	100.21

[a] By lactone method, A, from total saponification.

siderably less than the theoretical amount of chlorine, is soluble, indicating intramolecular lactonization. Upon forced lactonization (Tables II and III), intermolecular reaction occurs, with accompanying insolubilization. The intermolecular reaction probably occurs between carboxyl and chlorine units which have become isolated and have no γ- or δ-component along the chain for intramolecular reaction. Under proper conditions, intramolecular lactonization reaction supersedes the reaction between chains. The presence of an alcohol offers isolated carboxyls a reactable group to nullify the cross-linking reaction. The addition of sufficient water shifts the acid-ester equilibrium to the extent that cross-linking may again be possible. Dilution under constant water and alcohol ratio may also shift the acid-ester equilibrium though the mechanical separation alone may reduce the probability sufficiently.

The mechanism of the reaction cannot be determined from the available data. Hydrogen chloride would be the by-product whether the ring forms through interaction of halogen and carboxyl hydrogen, hydroxyl and carboxyl group, or the loss of hydrogen chloride from the chain followed by the addition of carboxyl to the double bond. Under the acid conditions present during the lactonization, the latter mechanism does not appear probable.

The residual halogen in the polymer offers a point for interesting speculation. Evidence not included here indicates an equilibrium between the halogen on the chain and the hydrogen chloride in the lactonizing solution, since removing the hydrogen chloride causes a reduction in the chlorine content of the polymer. The possibility of chlorine atoms isolated between rings without carboxyl groups with which to form lactones cannot be ignored. Such isolation of groups has been noted for other cyclizations in polymers.

Using the analytical methods described in this paper, the composition of the ester lactones of poly-α-chloroacrylic acid may be completely defined. Ester and lactone groups predominate with small amounts of carboxyl, hydroxyl and residual halogen groups.

Summary

1. Poly-α-chloroacrylic acid undergoes simultaneous esterification and lactonization when heated in solution in an alcohol.

2. The derived polymer contains carboxyl, hydroxyl, and residual chlorine groups in addition to the predominating lactone and ester groups.

3. Analytical methods for structural analysis of the ester-lactone polymer are described.

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