Patented Apr. 22, 1947

2,419,221

UNITED STATES PATENT OFFICE

2,419,221

COPOLYMERS OF 2-HALOGENO-ALLYL ALCOHOL OR 2-HALOGENO-ALLYL ESTERS

William O. Kenyon and John H. Van Campen, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application May 11, 1942, Serial No. 442,453

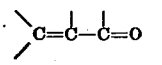
1 Claim. (Cl. 260—84)

1

This invention relates to copolymers of 2-halogeno-allyl alcohols or 2-halogeno-allyl esters.

2-halogeno-allyl alcohols and 2-halogeno-allyl esters are known, but all attempts to homopolymerize these substances to give useful resinous materials have so far failed. Certain esters of 2-chloro-allyl alcohol, viz. those containing at least two ethylenic linkages, e. g. 2-chloro-allyl crotonate and di-(2-chloro-allyl)-succinate, have been conjointly polymerized with compounds also containing an ethylenic linkage conjugated with another carbon to carbon double bond such as styrene, to give cross-linked polymers which usually have decreased solubilities in organic solvents. Certain other esters of 2-chloro-allyl alcohol, containing but one ethylenic linkage, viz. 2-chloro-allyl chloroacetate, have been proposed as "modifiers" in the polymerization of polymerizable organic compounds also containing but one ethylenic linkage, such as vinyl compounds and vinylidene chloride.

We have now found that 2-halogeno-allyl alcohols and 2-halogeno-allyl esters containing but one ethylenic linkage can be copolymerized with polymerizable organic compounds containing an ethylenic linkage conjugated with another double-bond linkage, e. g. an ethylenic or carbonylic linkage, to give useful resinous copolymers. Especially useful compounds are obtained with polymerizable organic compounds containing an ethylenic linkage conjugated with a carbonylic linkage, i. e. polymerizable organic compounds containing the group



It is, accordingly, an object of our invention to provide new resinous copolymers. Another object is to provide a process for preparing such copolymers. Other objects will become apparent hereinafter.

In accordance with our invention, we copolymerize 2-halogeno-allyl alcohols and 2-halogeno-allyl esters containing but one ethylenic linkage with polymerizable organic compounds containing an ethylenic linkage conjugated with another double-bond linkage. As 2-halogeno-allyl compounds, we prefer the more readily available, more stable 2-chloro-allyl compounds. As 2-chloro-allyl esters which we have found especially useful in practicing our invention, the following can be mentioned: 2-chloro-allyl esters of monobasic inorganic acids, such as hydrochloric acid, 2-chloro-allyl esters of monobasic carboxylic acids of the formula $C_nH_{2n+1}COOH$ wherein n represents a positive integer. As polymerizable organic compounds containing an ethylenic linkage conjugated with another double-bond linkage, the following can be mentioned: 1,3-butadiene, 2-chloro-1,3-butadiene, styrene, acrylic acids, e. g. acrylic

2

acid and α-substituted acrylic acids, such as methacrylic acid, ethacrylic acid and α-chloro-acrylic acid, esters of acrylic acids, e. g. methyl acrylate, isobutyl acrylate, methyl methacrylate, n-butyl methyacrylate and methyl α-chloro-acrylate.

The proportion of monomeric 2-halogeno-allyl compound to polymerizable organic compound containing an ethylenic linkage conjugated with another double-bond linkage can be any desired ratio. However, we have found that in the copolymer the ratio of 2-halogeno-allyl compound to the second compound is never greater than 1:1. More than one 2-halogeno-allyl compound can be copolymerized with one polymerizable organic compound containing an ethylenic linkage conjugated with another double-bond linkage, and more than one of the compounds containing the conjugated system can be employed with one 2-halogeno-allyl compound.

In general, we prepare our new copolymers as follows: the monomers are mixed in the desired ratio, a polymerization catalyst, e. g. an organic peroxide, added, and the resulting mixture allowed to polymerize, advantageously with warming. Any of the catalysts known to effect the polymerization of vinyl compounds can be employed. The resulting resin is dissolved in a suitable solvent, and the solution poured into a non-solvent for the resin (usually water) to precipitate the resin. The precipitated resin is then washed with water (and steamed, if necessary) and finally dried. The following examples and table will serve to illustrate the copolymers and the process for preparing them.

EXAMPLE 1.—COPOLYMER OF 2-CHLORO-ALLYL ALCOHOL AND METHYL-α-METHACRYLATE

A solution of 5 g. of methyl α-methacrylate, 5 g. of 2-chloro-allyl alcohol and 0.05 g. of benzoyl peroxide was prepared and placed in an Erlenmeyer flask. The flask was stoppered and placed in an oven at 40° C. After four and one-half months the mixture was found to be solid and slightly yellow in color. The product was dissolved in acetone and the solution diluted to 100 cc. with acetone. The diluted solution was filtered and then poured into cold water to precipitate the copolymer. The cream colored, fibrous precipitate was soaked for two hours, filtered and dried in the air at room temperature. The yield was 5.2 g. The copolymer contained chlorine equal to 8.27% by weight.

EXAMPLE 2.—COPOLYMER OF 2-CHLORO-ALLYL ALCOHOL AND STYRENE

A solution of 10.6 g. of styrene, 9.4 g. of 2-chloro-allyl alcohol and 0.2 g. of benzoyl peroxide were sealed in a glass tube and put into a water bath at 40° C. for fifteen days. The reaction

mixture was then diluted with an equal volume of dioxane and the diluted mixture poured into 700 cc. of methanol to precipitate the copolymer. The copolymer was dissolved in dioxane and the solution poured into water to precipitate the copolymer. The copolymer was filtered off and dried in the air at room temperature. The colorless, friable product weighed 2.5 g. and contained 2.6% by weight of chlorine.

Example 3.—Copolymer of 2-Chloro-allyl Alcohol and 2-Methacrylic Acid

A solution of 9.25 g. of 2-chloro-allyl alcohol, 8.6 g. of α-methacrylic acid and 0.2 g. of benzoyl peroxide was heated for thirty minutes in a steam bath. The resulting semi-solid mass was dissolved in acetone containing some water. The acetone solution was poured into distilled water to precipitate the copolymer. The copolymer was permitted to soak for two hours in the water and then was filtered off and dried in the air at room temperature. The slightly yellow, friable product weighed 9.2 g. and contained 7.85% by weight of chlorine.

Example 4.—Copolymer of 2-Chloro-allyl Chloride and Methyl α-Methacrylate

A solution of 50 g. of methyl methacrylate, 56 g. of 2-chloro-allyl chloride and 1.06 g. of benzoyl peroxide was prepared and heated on a steam bath. After twenty-seven and one-half hours heating, 1.06 g. of benzoyl peroxide were added to the yellow, viscous liquid. At the end of two further hours of heating, the reaction mixture was very viscous. Heating was discontinued and the reaction mixture dissolved in acetone. The acetone solution was poured into hot water to precipitate the copolymer. The copolymer was then steamed for five hours. The copolymer was redissolved in acetone and the acetone solution again poured into water to precipitate the copolymer. The copolymer was soaked in ethanol and again dissolved in acetone. The acetone solution was again poured into water to precipitate the copolymer. The copolymer was filtered off and dried at room temperature. The slightly yellow, friable product weighed 75 g. and contained 28% by weight of chlorine.

Example 5.—Copolymer of 2-Chloro-allyl Chloride and Styrene

A solution of 9.7 g. of styrene, 10.3 g. of 2-chloro-allyl chloride and 0.2 g. of benzoyl peroxide was sealed in a glass tube and the tube immersed in a water bath at 40° C. for fifteen days. The reaction product, a viscous liquid, was diluted with an equal volume of 1,4-dioxane. The resulting solution was poured into 700 cc. of methanol to precipitate the copolymer. The copolymer was permitted to soak in the methanol for some time. The copolymer was then redissolved in dioxane and reprecipitated by pouring the solution into water. The copolymer was filtered off and dried in the air at room temperature. The colorless, friable copolymer weighed 5.7 g. and contained 15.49% by weight of chlorine.

Example 6.—Copolymer of 2-Chloro-allyl Chloride and α-Methacrylic Acid

A solution of 11.2 g. of 2-chloro-allyl chloride, 8.6 g. of methacrylic acid and 0.2 g. of benzoyl peroxide was heated for one-half hour in a steam bath. The resulting semi-solid mass was dissolved in acetone containing some water. The copolymer was separated by precipitating the solution into cold water. After soaking for an hour in water, the copolymer was filtered off, and dried in the air at room temperature. The dried, colorless, friable product weighed 8.8 g. and contained 16.97% by weight of chlorine.

Example 7.—Copolymer of 2-Chloro-allyl Acetate and Methyl Acrylate

A solution of 12.8 g. of methyl acrylate, 20 g. of 2-chloro-allyl acetate and 0.078 g. of benzoyl peroxide was sealed in a glass tube and the tube was heated in a steam bath for three days. The reaction product was dissolved in acetone, the acetone solution poured into water and the precipitated copolymer steamed for five hours. The copolymer was redissolved in acetone, and the acetone solution poured into distilled water to precipitate the copolymer. The copolymer was permitted to soak in the water for some time and was finally filtered from the water. Copolymer was then dried in a desiccator under reduced pressure. The almost colorless copolymer was a bit friable and weighed 20 g. It contained 13.48% of chlorine.

Example 8.—Copolymer of 2-Chloro-allyl Acetate and Acrylic Acid

A solution of 20 g. of 2-chloro-allyl acetate, 10.7 g. of acrylic acid and 0.077 g. of benzoyl peroxide was heated under reflux on a steam bath for seventeen hours. The reaction product was immobile and amber in color. It was dissolved in acetone and the acetone solution filtered. The acetone solution was then poured into benzene to precipitate the copolymer which was dried in the air at room temperature. The slightly yellow, friable copolymer weighed 16 g. and contained 13.67% of chlorine.

Example 9.—Copolymer of 2-Chloro-allyl Acetate and Methyl Methacrylate

A solution of 13.45 g. of 2-chloroallyl acetate, 10 g. of methyl methacrylate, and 0.12 g. of benzoyl peroxide was prepared and sealed into a glass tube. The tube and contents were heated in a water bath at 50° C. for seventeen days, at the end of which time the product was hazy and faintly yellow. The copolymer was dissolved in acetone, the solution filtered, and the copolymer precipitated into water and soaked several hours in fresh water. It was then steamed for four hours, redissolved in acetone, precipitated into distilled water, and soaked in fresh distilled water. The product was dried in the air at room temperature. The colorless, friable material weighed 17.2 g. and contained 11.97% of chlorine.

Example 10.—Copolymer of 2-Chloro-allyl Acetate and Styrene

A solution of 13.45 g. of 2-chloroallyl acetate, 10.4 g. of styrene, and 0.12 g. of benzoyl peroxide was prepared and sealed into a glass tube. The tube and contents were heated in a water bath at 50° C. for twenty-one days, at the end of which time the product was very viscous, clear, and yellow in color. It was dissolved in dioxane, poured into distilled water, steamed for four hours, and redissolved in dioxane. This solution was precipitated into distilled water, the copolymer soaked for three hours, filtered, and dried in the air at room temperature. The colorless, friable product weighed 12.4 g. and contained 7.42% of chlorine.

The following table summarizes some of the more significant copolymerizations which have

been carried out in accordance with our invention.

Table

grams of 2-chloro-allyl compound	second monomeric compound, grams	grams of benzoyl peroxide	temp., ° C. and time of heating	per cent chlorine in polymer	mole ratio of 2-chloro-allyl compound to second compound in copolymer
2-CHLORO-ALLYL ALCOHOL COPOLYMERS					
9.25	α-methacrylic acid, 8.6	0.2	100, ½ hr.	7.85	1:4.18
92.5	α-methacrylic acid, 86	1.785	100, ¼ hr.	7.72	1:4.28
46.25	α-methacrylic acid, 21.5	0.68	100, 25 min.	11.61	1:2.48
46.25	α-methacrylic acid, 21.5	1.7	100, 3¼ hr.	12.42	1:2.24
46.25	α-methacrylic acid, 21.5	1.36	60, ¾ hr.	11.59	1:2.5
46.25	α-methacrylic acid, 21.5	1.36	70, 25 min.	12.5	1:2.23
46.25	α-methacrylic acid, 21.5	0.68	70, 30 min.	12.36	1:2.25
46.25	α-methacrylic acid, 21.5	0.68	65, 2 hrs.	11.86	1:2.41
5.0	methyl α-methacrylate, 5.0	0.05	40, 15 days	8.27	1:3.37
46.3	methyl α-methacrylate, 50	0.963	100, 27 hrs.	8.75	1:3.14
46	methyl-acrylate, 43	0.89	80, 22 hrs.	17.02	1:1.35
7.9	n-butyl α-methacrylate, 12.1	0.2	100, 2½ hrs.	6.47	1:3.21
7.9	n-butyl α-methacrylate, 12.1	0.2	40, 15 days	6.12	1:3.43
9.4	styrene, 10.6	0.2	40, 15 days	2.6	1:12.25
2-CHLORO-ALLYL CHLORIDE COPOLYMERS					
11.2	α-methacrylic acid, 8.6	none	60, 7 days	12.86	1:5.13
11.2	α-methacrylic acid, 8.6	0.2	100, ½ hr.	16.97	1:3.58
112.0	α-methacrylic acid, 86.0	1.98	100, 1 hr	19.33	1:2.98
11.1	α-methacrylic acid, 8.6	.0098	40, 10 days	16.9	1:3.6
11.1	α-methacrylic acid, 17.2	.0141	40, 10 days	13.23	1:4.95
56	methyl α-methacrylate, 50	1.06	100, 30 hr	28	1:1.43
56	methyl acrylate, 43	0.99	100, 46 hr.	32.2	1:1.27
8.8	n-butyl methacrylate, 11.2	0.2	40, 15 days	17.0	1:2.16
11.1	styrene, 10.4	0.107	40, 2 mo.	15.04	1:3.47
11.1	styrene, 20.8	0.0159	40, 2 mo.	11.28	1:5.1
10.3	styrene, 9.7	0.2	40, 15 days	15.49	1:3.34
2-CHLORO-ALLYL ACETATE COPOLYMERS					
20	acrylic acid, 10.7	0.077	100, 16.5 hr.	13.67	1:1.46
20	methyl acrylate, 12.8	0.078	100, 3 days	13.48	1:1.5
13.5	methyl acrylate, 17.2	0.07	100, 2 days	9.58	1:2.75

Our new copolymers, especially those in which the ratio of the 2-halogeno-allyl compound to the second compound is not greater than 1:3, are particularly useful as intermediates for the preparation of soluble materials which become insoluble upon separation from the solvent of a solution of the materials. (See the copending application of William O. Kenyon and William F. Fowler, Jr., Serial No. 442,452, filed of even date herewith.)

We have also found that 2-chloro-allyl acetate can be copolymerized with certain compounds which themselves are not polymerizable, such as maleic anhydride. The following example will serve to illustrate such a copolymer.

EXAMPLE 11.—COPOLYMER OF 2-CHLORO-ALLYL ACETATE AND MALEIC ANHYDRIDE

To a solution of 20.1 g. of 2-chloro-allyl acetate and 14.7 g. of maleic anhydride at 60° C. were added 0.07 g. of benzoyl peroxide. The resulting solution was heated in an oil bath at 120° C. After five minutes heating, the mixture underwent a slight reaction which quickly stopped. Also a yellow color appeared. The reaction mixture was cooled somewhat and 0.28 g. of benzoyl peroxide were added. The resulting solution was heated in the oil bath at 115° C. After five minutes heating, another vigorous, but short, reaction took place, and at the end of fifteen minutes the heating was stopped. The viscous-amber reaction product was dissolved in acetone, the resulting solution filtered, and the filtered solution poured into 750 cc. of benzene to precipitate the copolymer. The copolymer was permitted to soak for some time in the benzene. It was then filtered off and dried in the air. The slightly yellow friable product weighed 21.5 g. and was found to contain 14.89% of chlorine.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

A copolymer of 2-chloro-allyl acetate and acrylic acid containing 13.67 per cent of chlorine.

WILLIAM O. KENYON.
JOHN H. VAN CAMPEN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,160,941	Britton et al.	June 6, 1939
2,160,943	Britton et al.	June 6, 1939
2,186,360	Britton et al.	Jan. 9, 1940
2,205,390	Britton et al.	June 25, 1940
2,273,891	Pollack	Feb. 24, 1942
2,308,495	D'Alelio	Jan. 19, 1943
2,334,358	Smith	Nov. 16, 1943
2,332,897	D'Alelio	Oct. 26, 1943
2,332,900	D'Alelio	Oct. 26, 1943
2,332,460	Muskat	Oct. 19, 1943
2,388,851	Kenyon et al.	Nov. 13, 1945

FOREIGN PATENTS

Number	Country	Date
540,168	British	Oct. 8, 1941