

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE POLYMERIZATION OF ALKOXY-BUTADIENES

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No Drawing. Application filed August 23, 1940

The addition of alcohols to vinylacetylene is known. Thereby products were obtained being interpreted partly as butine derivatives, partly as allene derivatives and partly as alkoxy-2-butadienes. Useful polymers could not yet be produced out of these compounds. Experiments of polymerization were nearly always negative, compare e. g. Rothenberg Zentralblatt 1936, II, p. 1895.

We have now found, applying kallium-alcoholate as catalyst, a new class of alcohol addition products of vinylacetylene not known until now which surprisingly polymerizes easily. They have, as stated by us, the constitution of alkoxy-1-butadiene-1,3 of the general formula



whereby OR may be any kind of alcohol. By discovering effective catalysts used successfully for alkoxy-1-butadienes, we were able to realize the polymerization of alkoxy-2-butadienes. Mixtures of 1- and 2-alkoxy-butadienes are also polymerizable.

Specially suitable polymerization catalysts are kapillar-active substances like above all clay, kaolin and kapillaractive hydrosilicates known f. i. under the name of Tonasil, Frankonit, Floridin and the like. The polymerization is not accelerated by all of these substances, active carbon and silicagel scarcely act. As polymerization catalysts quite different substances however also may be used, especially some metal chlorides like FeCl₃, AlCl₃, ZnCl₂ and boron fluoride. Acids like hydrochloric acid, sulfuric acid, nitric acid, phosphorous pentoxide also cause polymerization. Elementary oxygen and the known peroxyde accelerators catalyze the polymerization. Further on the polymers themselves are polymerization catalysts. These catalysts can be employed as suspensions or solutions.

The properties of the polymerization products may be largely varied by means of the numerous methods applied in the art of polymerization of to-day, according to the intended use. Such means are f. i. the polymerization at defined temperatures with or without any solvents, the polymerization of the monomeric compound in an emulsified state, the polymerization of the monomeric compound with other polymerizable substances or with substances not polymerizing per se, the polymerization in the presence of polymers of other substances and the variation of the amount and composition of the polymerization catalysts and so on.

Above all it is important that there is the possibility of polymerizing the alkoxy-1-butadienes

with substances polymerizing per se as f. i. acrylic nitril, 1- and 2-acetoxy-butadiene, linseed oil or also with such ones polymerizing only in special cases together with other substances, as f. i. maleic anhydride. The reaction of alkoxy-2-butadiene with maleic acid anhydride has already been tried, obviously with the intention to perform a "diene-synthesis", but only a dark resin was obtained thereby under violent reaction. By the method of working applied by us, however, light elastic interpolymers are obtained with 1- and 2-alkoxy butadiene which according to the presence of functional groups may further be converted into derivatives of carbon acids. Partly the polymers are also oils with drying properties. In many cases the polymers are rubberlike, that is they are vulcanizable; they can chiefly be applied in the lacquer-industry and for artificial resins. The interpolymers comprise the whole scope of artificial resins which are oillike, rubberlike and resinlike.

Example 1

0.1 g of fine powdered kaolin are added to 10 g of ethoxy-butadiene at room temperature. The polymerization begins slowly; the temperature rises and solid polymerization products are precipitated. The temperature rises to the boiling point and the heat is removed by cooling. After few minutes the polymerization is finished. The polymer is a colorless till slightly yellow, rubberlike and slightly sticky mass which can be vulcanized by sulfur or other suitable means.

The ability of polymerizing depends on the purity of the ethoxy-butadiene that is the inclination of the product to polymerize increases with the increasing purity of the product. Butadiene ethers too react in the same way. The activity of the catalyst may be increased by previous heating; unglazed, burnt clay is a suitable catalyst too. The polymerization with pure substances and high active kaolin, used as catalyst, proceeds so violently that larger amounts overheat themselves until decomposition, if the reaction heat is not removed. The thus obtained polymers are for the most part very high molecular and unsoluble but swellable in solvents. Low molecular constituents can be extracted by ether. The course of the polymerization may be moderated by the addition of solvents.

In the same way alkyl-homologs of the ethoxy-1-butadiene may be polymerized f. i. methoxy-, propoxy-, butoxy-butadiene and the like. The polymerization is scarcely influenced by anti-oxidation catalysts as f. i. hydroquinone. The

methoxy-1-butadiene, boiling point: 87.5° C/703 mm D₄²⁰:0.8296, polymerizes somewhat more slowly than the ethyl derivative which shows the greatest ability of polymerizing. The polymerization velocity of the ethers with higher alkyl groups decreases when the alkyl groups increase.

Example 2

In a vessel, equipped with a stirrer, 50 parts by weight of benzene together with 0.6 parts by weight of kaolin are heated up to the boiling point and a mixture of 10 parts by weight of ethoxy-1-butadiene and 30 parts by weight of benzene are added dropwise. After 15 minutes a white gel-like mass begins to precipitate. The reaction is finished after a further hour. The solvent may be removed by water steam or by distillation. The remaining polymer is a nearly colorless, elastic mass. Instead of benzene other solvents such as ethyle acetate, carbon tetrachloride, methylene chloride and others may be used.

Example 3

Hexoxy-1-butadiene is solved in the same amount of benzene and heated with 1% of Floridin till to the boiling point. The working up takes place as shown in Example 2. A light elastic mass is obtained.

Example 4

Ethoxy-1-butadiene is heated with 0.5% of zinc chloride to 60° C under stirring. The resulting polymer is a thick, tough mass. Salts like aluminium chloride, iron chloride and other react similarly. The polymers are partly soluble, for the most part, however, they are insoluble in the usual solvents like benzene, acetone, alcohol, ethylacetate, and the like.

Example 5

1% of kaolin is added to ethoxy-2-butadiene and heated up in a pressure vessel to 100° C for 8 hours. A rubberlike polymer is obtained.

Example 6

2% of kaolin are added to a mixture of 9 parts by weight of ethoxy-1-butadiene and 1 part by weight of ethoxy-2-butadiene.

The polymerization is started by heating whereby the temperatures of the reaction must not be allowed to rise above 80°. When the temperature begins to decrease the polymerization by heating. The polymer is a light elastic mass.

Example 7

A molar amount of maleic anhydride is added to a solution of butoxy-1-butadiene in the double volumen of benzene; the mixture is heated whereby the sulfur-yellow solution becomes colorless. The very viscous solution yields after the evaporation of the benzene a rubberlike elastic mass. The polymer is vulcanizable.

Without diluents the alkoxy-1-butadiene react so violently with maleic anhydride that decomposition takes place. The reaction may easily be regulated by the addition of inert diluents. The interpolymers with larger alcohol groups show better solubility than those with smaller ones. The solubility also depends on the course of reaction and the after-treatment. If the solution is evaporated by a higher temperature the products cannot be solved in such an easy manner. Products being soluble in a specially easy manner are obtained if the reaction is executed rapidly and

with few solvents. The polymers swell extraordinarily well in lyes; the low molecular products yield high viscous solutions. The anhydride groups of the polymers can be converted with compounds reacting generally with anhydride as f.i. alcohols, amines and the like, whereby derivatives of the interpolymers are obtained. By this way the properties of the polymers may be varied.

Example 8

Molar amounts of ethoxy-1-butadiene and maleic anhydride are polymerized in the same amount of benzene as in Example 7. Hereafter an amount of ethylene glycol, corresponding with 1 mol, is added and the mixture is boiled under reflux as long as a homogeneous solution is obtained. By evaporating the solvent the ester of the interpolymer is obtained.

Example 9

In a vessel equipped with a stirrer are 5 parts by weight of boiling benzene and 0.06 parts by weight of kaolin. A mixture of 10 parts by weight of ethoxy-1-butadiene and a solution of 1 part by weight of maleic anhydride in 11 parts by weight of benzene is added dropwise. The polymerization is finished after 1 hour. A product of rubberlike properties is obtained after evaporating the solvent.

Example 10

Ethoxy-2-butadiene is brought to reaction with maleic anhydride in a boiling etheric solution. At the beginning of the reaction the solution is intensively yellow but when the polymerization proceeds the solution becomes more and more lighter. A high elastic product is obtained after evaporating the solvent at 100°. Another course of polymerization runs as follows: ethoxy-1-butadiene is solved in the same volume of benzene and the molar amount of maleic anhydride is added. After standing for 24 hours the yellow color disappears and a thick solution of the nearly colorless interpolymer is obtained.

Example 11

A slow current of oxygen is conducted at room temperature through butoxy-1-butadiene. After 12 hours a polymer in form of a thick colorless oil is obtained out of which still some monomeres may be removed by water steam. The oil has the property of drying and yields with the usual siccatives hardening films. Similar products are also obtained by the other alkoxy-1-derivatives of butadiene. The alkoxy-2-derivatives react correspondingly. The ethyl-glycol-ethers of the oxy-1-butadiene (boiling point 66-67°/9 mm D₄²⁰: 0.8970, of intensive odor of cress) and the oxy-2-butadiene (boiling point 54-55°/9 mm D₄²⁰: 0.8983, of aromatic odor but quite different from the odor of the 1-derivative) polymerize in a specially easy manner under the influence of air oxygen.

Example 12

Ethoxy-1-butadiene is boiled with 0.5% of benzoyl peroxyde. After 30 hour a viscous fluid is obtained still containing somewhat unpolymers ether.

Example 13

Pure ethoxy-1-butadiene is heated up to 120° in a pressure vessel. After 5 hours a thick colorless oil is obtained which is formed within a shorter time if the temperatures are higher.

Example 14

Oxygen is conducted at room temperature through cyclohexoxy-1-butadiene and the mixture is allowed to stand. After 3 days a thick colorless oil is obtained.

Example 15

1- α -Ethyl-hexoxy-butadiene is shortly treated with oxygen as shown in Example 14 and hereafter heated up to 100°. After some hours a thick colorless oil is obtained. The same result is obtained with the n-hexoxy-derivative.

Example 16

100 parts by weight of ethoxy-1-butadiene are

5 stirred with 200 parts by weight of petrolether and 1 part by weight of kaolin at 0°. After 3 days the essential amount is polymerized. The white polymer, unsoluble in petrolether, is separated from petrolether and extracted with new one.

Example 17

10 Ethoxy-1-butadiene is heated up to 130° with half the amount of acrylic-nitril in a closed vessel for 6 hours. A thick oil of a slightly yellow color is obtained.

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