

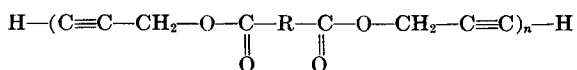
## Acetylenic Polyesters

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### Synopsis

Acetylenic polyesters containing either residues of 2-butyne-1,4-diol, acetylenedicarboxylic acid, or both of them, were prepared and characterized. Polyesters of 2-butyne-1,4-diol with succinic, adipic, and phthalic acids were obtained as soluble polymers by use of known methods. The polymaleate ester of 2-butyne-1,4-diol was obtained either as a soluble or as an insoluble polymer, depending on the experimental conditions. Relatively high temperature or long reaction periods led to the formation of insoluble polymers. Polyesters of acetylenedicarboxylic acid with diethylene glycol, tetra- and hexamethylene glycols, 2-butene-1,4-diol, and 1,4-cyclohexane dimethanol were prepared by melt polycondensation in bulk. These polyesters were obtained as insoluble, rubbery materials, except those of 2-butene-1,4-diol and 1,4-cyclohexane dimethanol, which were obtained both as linear or as nonlinear polymers. The insolubility of the polyesters of acetylenedicarboxylic acid was due to crosslinking reactions involving the conjugated system  $-\text{C}\equiv\text{C}-\text{C}=\text{O}$ . While the melt polycondensations in bulk involving either 2-butyne-1,4-diol or acetylenedicarboxylic acid were entirely controlled reactions, those carried out between acetylenedicarboxylic acid and 2-butyne-1,4-diol were very often associated with highly exothermic decompositions involving carbonization. The decompositions could be eliminated when the melt polycondensation in bulk was preceded by a fore-condensation in solution. Solid, soluble, powdery low polymers ( $\text{DP} = 2-3$ ) having softening temperatures of about  $150-175^\circ\text{C}$ . were thus obtained.

A large number of linear polyesters have been synthesized<sup>1</sup> since the pioneering work of Carothers and co-workers.<sup>2</sup> In spite of the wide scope of the field only a few linear polyesters containing triple bonds were prepared. Marvel and Johnson<sup>3</sup> prepared polysebacate of 2-butyne-1,4-diol by direct esterification and also by transesterification with the dimethyl ester and compared the physical properties of the polymer to those of the derived saturated polyester. Batzer and Weisenberger<sup>4,5</sup> synthesized the polyesters of acetylenedicarboxylic acid with hexa-, hepta-, and decamethylene glycols<sup>4</sup> by carrying out the polycondensation in solution.<sup>6</sup> Recently, Sladkov et al.<sup>7</sup> reported the synthesis of acetylenic polyesters by the oxidative coupling of the dipropargyl esters of maleic, succinic, and isophthalic acids to give polyesters of the type



where R is the residue of the acid.

The preparation of linear unsaturated polyesters in which the unsaturated carbon is adjacent to a carbonyl group, is complicated by side reactions leading to crosslinking.<sup>8-11</sup> It was the purpose of the present work to find out the optimal general conditions for the polymerization leading to the formation of acetylenic polyesters with the elimination of crosslinking and to overcome the great sensitivity<sup>12</sup> associated with the acetylenic starting materials and polymeric products. In this connection we investigated the preparation of linear polyesters based on either acetylenedicarboxylic acid or butyne-1,4-diol, as well as a polyester consisting of both of them. Polyesters containing triple bonds in both the diacid and glycol residues have not yet been reported. Polyesters containing the residue of either 2-butyne-1,4-diol or acetylenedicarboxylic acid alone were prepared in order to study separately the behavior of each of the acetylenic compounds under various experimental conditions used for the polycondensation reaction, before applying the polycondensation for both of them together.

Acetylenic polyesters might also be of great interest and importance as regards the relationship between chemical structure and physical properties of high polymers.<sup>13,14</sup>

## RESULTS AND DISCUSSION

### Preparation of Polyesters of 2-Butyne-1,4-diol

The polyesters of 2-butyne-1,4-diol with succinic, adipic, phthalic and maleic acids were prepared by known methods, such as direct polyesterification and reaction between the glycol and the acid anhydride. The polymerization was carried out under pure dry nitrogen in two stages. A mixture of the glycol and the acid or its anhydride (1-1.2:1 molar ratio) was first heated for 2-8 hr. at 180-190°C. under atmospheric pressure. During this period water distilled out and viscous low polymers were formed. The polymerization was then continued under vacuum (1-10 mm. Hg) for another 10-20 hr., during which excess of the glycol distilled out and higher polymers were formed.


The polyesters of the above first three saturated acids were obtained as linear polymers soluble in various solvents. Molecular weights, softening points, and solubilities are recorded in Table I. Whereas these linear soluble polyesters were obtained even under relatively drastic experimental conditions, milder conditions were required for the formation of linear soluble polymaleate esters.

Polycondensations leading to formation of maleic acid polyesters suffer from side reactions involving the carbonyl conjugated carbon-carbon double bond, which results in crosslinking.<sup>8,9</sup> This side reaction is affected mainly by heat, and is strongly accelerated by oxygen.<sup>8,9</sup> The effect of oxygen can be prevented by using antioxidants. The polycondensation of 2-butyne-1,4-diol with maleic acid or maleic anhydride was carried out under various experimental conditions in a nitrogen atmosphere.

TABLE I

Polyesters of 2-Butyne-1,4-diol



Expt. no.	Polyester R	Solubility	Softening temp., °C.	COOH		$\bar{M}_n$	$n$	Calcd. <sup>a</sup>		Found	
				value, mg. NaOH/g. polymer	OH value, mg. NaOH/g. polymer			C, %	H, %	C, %	H, %
19	$-\text{CH}_2-\text{CH}_2-$	Sol.: chloroform, DMF, DMSO Insol.: acetone, nitrobenzene, THF	40	12.9	11.1	3330	19.8	56.8	4.8	56.8	5.2
21	$-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2-$	Sol.: acetone, chloroform, DMF, THF	40-44	30.2	10.5	1970	10.0	60.7	6.2	60.4	6.1
18 <sup>b</sup>	$-\text{CH}_2(\text{CH}_2)_6-\text{CH}_2-$	Insol.: ethanol, benzene Sol.: chloroform, nitroethane, DMF	54	30.9	4.9	2240	8.8	66.1	8.0	65.8	8.2
22		Insol.: ethanol, benzene Sol.: acetone, chloroform, DMF Insol.: methanol	Viscous product	14.9	1.7	4820	22.3	66.1	3.7	64.0	4.0
8	$-\text{CH}=\text{CH}-$	Sol.: acetone, DMF Insol.: chloroform, toluene	Viscous product	124.7	85.2	381	2.3	—	—	—	—

<sup>a</sup> The elementary analyses were calculated for whole values of  $n$ .<sup>b</sup> The polysebacate ester was prepared according to Marvel and Johnson.<sup>3</sup>

It was found that the linearity or nonlinearity of the maleate polyesters obtained was not dependent on the presence of antioxidants, such as *N*-phenyl naphthylamine or hydroquinone, but was, however, dependent on reaction time and temperature. Relatively high temperatures and long reaction times resulted in nonlinear polyesters which were insoluble in dimethylformamide. Even at relatively low reaction temperatures, linear soluble polyesters were converted into insoluble ones on increasing the reaction time. This occurred at a certain defined stage of the reaction. In one experiment, for example, the polyester was soluble until its carboxyl value reached a value of 100 mg. NaOH/g. polymer, whereafter crosslinking took place. Such a behavior was also observed by Vincent<sup>9</sup> and Kohn.<sup>12</sup>

The following experimental conditions were suitable for preparing linear polymaleate-2-butyne esters: (a) heating an equimolar mixture of the glycol and maleic acid at 160–180°C. for 90 min. (b) heating the above mixture at 130–150°C. for 4–9 hr.; (c) heating an equimolar mixture of the glycol and maleic anhydride at 135–145°C. for 3–6 hr.

### Preparation of Polyesters of Acetylenedicarboxylic Acid

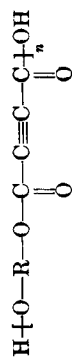
Polyesters of acetylenedicarboxylic acid and of the following diols were prepared: (a) diethylene glycol, (b) tetramethylene glycol, (c) hexamethylene glycol,\* (d) 2-butene-1,4-diol, (e) 1,4-cyclohexane dimethanol, (f) 2-butyne-1,4-diol. The polyesters of the glycols (a–e) were prepared by direct melt polyesterification. Experimental difficulties existed in the synthesis and isolation of these acetylenic polyesters, which were similar to those encountered in the case of the polyesters of maleic acid. This was the "drying" phenomenon—the conversion of a linear soluble polyester to an insoluble, nonlinear one.<sup>8</sup> Batzer and Weisenberger<sup>5,6</sup> already noticed that in the course of removal of solvent from their solutions, acetylenedicarboxylic acid polyesters were converted into insoluble polymers. This "drying" phenomena of the polyesters of acetylenedicarboxylic acid is to be attributed to the existence of the  $-\text{C}\equiv\text{C}-\text{C}=\text{O}$

conjugated system. This system might be responsible for the reactions leading to crosslinking, in analogy to the  $-\text{C}=\text{C}-\text{C}=\text{O}$  system in the case of the polymaleate esters.

The polyesterifications were carried out under nitrogen in order to prevent crosslinking due to oxygen convertibility. Heat convertibility could not be entirely eliminated, although relatively low temperatures (80–140°C.) were used. Much higher temperatures could not be used, as acetylenedicarboxylic acid decomposes at 179°C. The general method employed for the preparation of the polyesters of the glycols (a–e) was

\* Poly(hexamethylene-acetylenedicarboxylate) has already been prepared<sup>5,6</sup> by polycondensation in solution.

TABLE II  
Polyesters of Acetylenedicarboxylic Acid



Expt. no.	Polyester R	Solubility	Softening temp., °C.	COOH value, mg. NaOH/g. polymer	OH value, mg. NaOH/g. polymer	Calcd. <sup>a</sup>		Found		
						n	C, %	H, %	C, %	H, %
27	$-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$	Insol. <sup>b</sup> <i>m</i> -cresol, dichloroacetic acid, DMF, trifluoroacetic acid	—	26.8	31.8	7.4	51.5	4.4	49.5	4.9
47	$-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2-$	Insol. <sup>b</sup> <i>m</i> -cresol, dichloroacetic acid	—	2.5	1.7	113.4	57.1	4.8	55.6	5.0
30	$-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2-$	Insol.: <i>m</i> -cresol, dichloroacetic acid, chloroform, acetone, DMF	—	3.0	7.3	39.6	61.1	6.1	60.6	6.3
64	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$	Sol.: acetone, DMF, DMSO Insol.: <i>m</i> -cresol, dichloroacetic acid, trifluoroacetic acid	—	36.3	38.5	6.4	56.8	3.8	56.9	4.5
29	$-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$	Sol.: chloroform, dioxane, THF Insol.: acetone, nitroethane, DMF	80-120	6.0	12.5	4324	64.6	6.3	64.8	6.6

<sup>a</sup> Calculated for whole values of *n*.

<sup>b</sup> A yellow, nonlinear, insoluble, spongy, rubbery product was obtained.

<sup>c</sup> Became insoluble after storage for one month under vacuum.

as follows. A 1:1 molar mixture of the acid and the glycol was heated at constant temperature (80°C.) for 9–48 hr. under nitrogen at atmospheric pressure. It was further heated at 80–140°C. (1–690 mm. Hg) for 4–12 hr. The polyesters of diethylene glycol and tetra-, and hexamethylene glycols were obtained as yellow, spongy, rubber-like insoluble materials, whereas the polyesters of 1,4-cyclohexane dimethanol and of 2-butene-1,4-diol were obtained both as linear powdery soluble polymers and as insoluble ones, depending on the polymerization conditions. The linear polyesters of 2-butene-1,4-diol changed to insoluble ones on storage under vacuum at room temperature for one month. The linear polyesters of 1,4-cyclohexane dimethanol showed a greater resistance to crosslinking and remained linear even after long storage periods. It should be emphasized in this connection that whereas soluble linear polyesters were obtained from 2-butene-1,4-diol and various diacids (Table I), most of the polyesters prepared from acetylenedicarboxylic acid were insoluble (or became insoluble) similar to the polyesters of maleic acid. Some of the properties of the polymers, molecular weights, and analytical data are presented in Table II.

### Preparation of Polyesters of Acetylenedicarboxylic Acid and Butyne-1,4-diol

In addition to the difficulties encountered in preparing linear acetylenic polyesters which were due to the conjugated systems  $-\text{C}=\text{C}-\text{C}=\text{O}$  and  $-\text{C}\equiv\text{C}-\text{C}=\text{O}$ , other great experimental difficulties arose due to the

high energy content of the above acetylenic diol and diacid starting materials and polymeric products. Because of the great accumulation of reactive unsaturated centers, the reaction mixture was relatively very sensitive, and spontaneous highly exothermic decompositions involving carbonization occurred very often. To eliminate these decompositions three methods of preparation were examined: direct polyesterification, direct polyesterification in the presence of antioxidants, and a two-stage polycondensation consisting of a fore-condensation in the first stage to give low condensates, which were further condensed in the second stage to higher polymers.

In the first method, an equimolar mixture of the diol and the diacid was kept under nitrogen at 60°C./690 mm. Hg. This method proved to be inefficient, since decomposition occurred within 15–240 min. from the beginning of the reaction in 11 out of 13 experiments carried out. The decompositions occurred mainly towards the end of the dissolution of the acid in the melted diol. In a modification of this method the reactants were dissolved in a minimal quantity of acetone in order to homogenize the reaction mixture and heated under reflux in a nitrogen atmosphere for 15–60 min. The acetone was distilled out and the reaction mixture was

heated at 80°C. to continue the condensation. This modification improved the results since decompositions occurred only in three experiments out of the eight carried out. However, this modification was useful only for small-scale preparations, as the solubility of the acid was small as compared to that of the diol, so that it separated out as a solid on removal of the acetone.

In the second method, the direct polyesterification was carried out in the presence of antioxidants (*N*-phenyl-2-naphthylamine, *p*-hydroquinone, 2,5-di-*tert*-butyl hydroquinone) to establish whether the decomposition was caused by an oxidation reaction involving radicals. An equimolar mixture of the diol and the diacid together with the antioxidant (5 mole-%) were kept under nitrogen at 80°C./690 mm. Hg for 4–26 hr. This was found to be partially efficient. Although no decompositions occurred in four out of the eight experiments carried out, the temperature inside the reaction mixture rose temporarily up to 150–160°C., indicating that there was an exothermic side reaction which was not followed by decomposition. This behavior might be ascribed to the antioxidant present.

The only method which proved to be efficient was the third one in which, in the first stage an equimolar mixture of diol and the diacid was dissolved in dioxane, acetone, or tetrahydrofuran (20 g./100 ml. solvent) and the solution refluxed for 24 hr. The solvent was then distilled out and the viscous residue was heated for 20–24 hours at 80°C./690 mm. Hg, and for an additional 4 hr. at 80°C./5–70 mm. Hg, during which the reaction mixture solidified. No decompositions occurred in the eight experiments carried out. Only low polymers having 2–3 segments could be obtained, since the polymers were infusible at the temperature used, and higher temperatures led to decompositions.

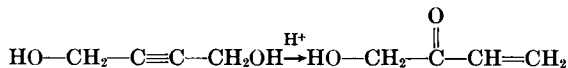
The polymers obtained from 2-butyne-1,4-diol and acetylenedicarboxylic acid were soluble in acetone, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and insoluble in ether, chloroform, and water. They had relatively high softening points (150–175°C.) even though their degree of polymerization was low ( $n = 2-3$ ). This was in contrast with the low softening temperatures obtained with the other linear acetylenic polyesters prepared. It seems that the high rigidity of the triple bonds of the diacid and the glycol is responsible for this behavior.

The fact that soluble polymers were obtained from the above acetylenic diol and diacid is interesting and somewhat surprising, as most of the polyesters prepared from acetylenedicarboxylic acid were insoluble (Table II) and their tendency to crosslinking was already noticed by Batzer and Weisenberger.<sup>4,5</sup> Bradley<sup>8</sup> and co-workers have shown that polyesters of maleic acid undergo crosslinking after attaining a certain minimal chain length. In our case, the very short chain length obtained ( $n = 2-3$ ) may similarly be responsible for the lack of crosslinking.

It was shown that the polyesterifications in bulk, carried out with either 2-butyne-1,4-diol or acetylenedicarboxylic acid were entirely controlled reactions (Tables I and II), in contrast with the bulk polyesterifications

carried out with both of them together, which were generally uncontrollable and accompanied by complete decomposition and carbonization. This indicated that there was some mutual influence of the acetylenic diol and diacid used which caused these violent reactions.

It is known<sup>15</sup> that 2-butyne-1,4-diol readily undergoes the Meyer-Schuster rearrangement in the presence of strong acids to form hydroxymethyl vinyl ketone:



The reaction is strongly exothermic. Acetylenedicarboxylic acid present in the reaction mixture is a very strong acid ( $pK_a = 1.74$ )<sup>16</sup> as compared to the other investigated diacids, and it caused such a rearrangement of the butyne diol. This was supported by the fact that small quantities of hydroxymethyl vinyl ketone distilled out during the exothermic decompositions. The heat evolved in this rearrangement seems to be the cause for the uncontrollable reactions by decomposing the acetylenedicarboxylic acid (which is decomposed at 180°C.). The temporary rise of temperature (up to 150–160°C.) found in some of the bulk polyesterifications carried out in the presence of antioxidants might be due to such a rearrangement, which took place to a certain extent.

NMR spectra of the soluble poly acetylenedicarboxylate of 2-butyne-1,4-diol prepared by using the fore-condensation method did not show the presence of any ( $\text{CH}_2=$ ) hydrogens. This confirmed that no hydroxymethyl vinyl ketone residue was incorporated in the polymer.

The infrared spectra of all the acetylenic polyesters prepared showed no absorption band for the  $\text{C}\equiv\text{C}$  bond, the same as was already noticed by Marvel and Johnson.<sup>3</sup> This might be explained by the symmetry of the polymer as regards the triple bond.<sup>17</sup>

The polyesters were purified by precipitation from solution. Polyesters which precipitated directly as a fine granular precipitate gave good elementary analytical results; polyesters such as, the polyphthalate and polyacetylenedicarboxylate of 2-butyne-1,4-diol which precipitated as viscous materials that solidified only on standing in the cold, showed deviations in their elementary analyses. The analyses of the polyacetylenedicarboxylate esters of 2-butyne-1,4-diol gave high values of per cent hydrogen. This might be due to trapped water molecules, which could not be removed under nondestructive conditions. Such a behavior was already noticed in the case of other polyesters.<sup>2</sup>

## EXPERIMENTAL

### Materials

Acetylenedicarboxylic acid was prepared from the potassium salt<sup>18</sup> and was recrystallized several times from ether-petroleum ether. Norite was used to remove the color. It was dried *in vacuo* over phosphorus



pentoxide, m.p. 178–179°C. 2-Butyne-1,4-diol (B.D.H.) was dissolved in hot ethyl acetate, the color removed with Norite, and precipitated in the cold with toluene. This process was repeated several times until a pure crystalline product, m.p. 57–58°C., was obtained.

Other diacids and glycols used were recrystallized or fractionally distilled before use.

Pyridine, a high purity grade, was refluxed for 5 hr. over sodium hydroxide pellets and fractionally distilled.

Triethylamine was refluxed for 5 hr. over sodium hydroxide pellets; the fraction boiling at 87–88°C./690 mm. Hg was used. Acetic anhydride was fractionally distilled.

The acetylation reagent was prepared by dissolving acetic anhydride (0.3 ml.) in 250 ml. of either pyridine or triethylamine.

### Determination of Molecular Weights

Number-average molecular weights were determined from the hydroxyl and carboxyl endgroups of the polyesters. The carboxyl value<sup>19</sup> was the weight number of milligrams of NaOH required to neutralize the carboxyl endgroups in 1 g. polymer. The hydroxyl value was the weight (in milligrams) of NaOH equivalent to the quantity of acetic acid used in the acetylation of the hydroxyl groups present in 1 g. polymer. The molecular weight was calculated as follows:<sup>19</sup>

$$\frac{\text{Hydroxyl value} + \text{carboxyl value}}{2 \times 40 \times 1000} = \text{moles of polymer per gram}$$

$$\text{Molecular weight} = 1/\text{moles of polymer per gram}$$

The procedure given by Sorensen and Campbell<sup>19</sup> for the determination of carboxyl and hydroxyl endgroups was used with some modifications.

The carboxyl value was determined by direct titration of the polymer suspended in water, acetone, dimethylformamide, or pyridine with aqueous sodium hydroxide solution, phenolphthalein being used as indicator. This indicator could not be used in the determination of the carboxyl value of the polyesters of acetylenedicarboxylic acid with tetramethylene and hexamethylene glycols, and with 2-butene-1,4-diol and 2-butyne-1,4-diol, since the solutions of these polymers were colored. Anhydrous titrations<sup>20</sup> by sodium methoxide or Triton B were therefore carried out using thymol blue as indicator, the polymers being suspended in dioxane or triethylamine, respectively.

The hydroxyl value was determined by using the pyridine-acetic anhydride acetylation reagent.<sup>19</sup> However, very dark solutions were obtained with the use of this acetylation reagent in the case of polyphthalate and polymaleate esters of 2-butyne-1,4-diol and in the case of the polyacetylenedicarboxylate esters of diethylene, tetramethylene, and hexamethylene glycols, 1,4-cyclohexanedimethanol, 2-butene-1,4-diol, and 2-butyne-1,4-diol. To overcome this difficulty, triethylamine-acetic anhydride was

used as an acetylation reagent. The acetylation was carried out at reflux temperature for 2 hr. When this reagent was used, hydrolysis of excess acetic anhydride was not necessary, since it could be titrated directly by a solution of Triton B with thymol blue as indicator.<sup>20</sup> Determination of the hydroxyl groups of 2-butyne-1,4-diol with the use of this reagent gave good reproducible results.

### Polycondensation Procedure

The polycondensation was carried out in a reaction vessel which was composed of a three-necked flask fitted with a condenser for downward distillation, an adapter for introducing nitrogen, and an opening through which samples can be removed during the reaction. The reaction vessel was sealed in an external vessel having an opening fitted with a reflux condenser. The temperature inside the reaction vessel was determined by the vapors of the boiling liquid in the external vessel. The polycondensations were carried out in a pure dry nitrogen atmosphere.

**Polysuccinate of 2-Butyne-1,4-diol.** A mixture of 2-butyne-1,4-diol (3.44 g., 0.04 mole) and succinic anhydride (3.3 g., 0.033 mole) was heated at 180°C. under atmospheric pressure (690 mm.) for 2.5 hr., under 2–4 mm. pressure for 10 hr., and under 1 mm. pressure for another 10 hr. The polyester melt obtained was dark brown. The polymer was dissolved in hot chloroform (25 ml.), filtered, and precipitated with acetone (25 ml.). The polyester precipitated on cooling as a fine light brown powder.

**Polyadipate of 2-Butyne-1,4-diol.** A mixture of 2-butyne-1,4-diol (3.44 g., 0.04 mole) and adipic acid (4.88 g., 0.033 mole), was heated at 186°C. under atmospheric pressure for 3.5 hr. and under 1 mm. pressure for 18 hr. more. The polymer was dissolved in hot acetone (50 ml.), filtered, and precipitated with a small quantity of water. The polyester precipitated as a fine powder.

**Polyphthalate of 2-Butyne-1,4-diol.** A mixture of the diol (3.44 g., 0.04 mole) and phthalic anhydride (4.94 g., 0.033 mole) was heated at 186°C. under atmospheric pressure for 8 hr. (during this stage besides water, a small quantity of phthalic anhydride distilled out) and under 7–12 mm. pressure for 12 hr. more. The polymer melt obtained was dark brown. The polymer was dissolved in hot chloroform, filtered, and evaporated to dryness *in vacuo*. It was obtained as a brown plastic material which did not solidify at room temperature

**Polyacetylenedicarboxylate of 1,4-Cyclohexane Dimethanol.** Acetylenedicarboxylic acid (3.42 g., 0.03 mole) and 1,4-cyclohexane dimethanol (4.3 g., 0.03 mole) were heated at 80°C. under atmospheric pressure for 7 hr. and under 30–40 mm. pressure for 2 hr. more. The polymer was dissolved in chloroform (300 ml.), filtered, and evaporated to dryness. The solid residue was triturated with petroleum ether and filtered; a white soluble polymer was obtained.

In an alternative procedure, a mixture of acetylenedicarboxylic acid (3.211 g., 0.0284 mole) and 1,4-cyclohexane dimethanol (4.056 g., 0.0284 mole) was heated at 80°C. under atmospheric pressure for 9 hr. and under a pressure of 60–90 mm. for 5 hr. more. The temperature was raised to 110°C., and the reaction mixture was further heated for 5 hr. at a pressure of 35 mm. A mixture of soluble and insoluble polymers was obtained which was separated by extraction with hot chloroform. The insoluble polymer is a spongy, light-yellow material which is insoluble in *m*-cresol, dichloroacetic acid, or trifluoroacetic acid.

**Polyacetylenedicarboxylate of Diethylene Glycol.** Acetylenedicarboxylic acid (6.003 g., 0.0527 mole) and diethylene glycol (5.588 g., 0.0527 mole) were heated under atmospheric pressure at 80°C. for 36 hr., at 110°C. for 2.5 hr., and at 140°C. at a pressure of 17 mm. for a further 1.5 hr. The yellowish spongy polymer was insoluble, and it was purified by washing with methanol and ether.

**Polyacetylenedicarboxylate of Hexamethylene Glycol.** Acetylenedicarboxylic acid (4.56 g., 0.04 mole) and hexamethylene glycol (4.72 g., 0.04 mole) were heated under atmospheric pressure at 80°C. for 24 hr., at 110°C. for 4 hr. and at a temperature of 140°C. and a pressure of 5 mm. for 4 hr. more. The polymer was spongy and insoluble.

**Polyacetylenedicarboxylate of Tetramethylene Glycol.** Acetylenedicarboxylic acid (6.464 g., 0.0566 mole) and tetramethylene glycol (5.1 g., 0.0566 mole) were heated at 80°C. under atmospheric pressure for 48 hr. The yellowish spongy polymer obtained was insoluble. It was purified by trituration with methanol and with ether.

**Polyacetylenedicarboxylate of 2-Butene-1,4-diol.** A mixture of the diacid (5.54 g., 0.0486 mole) and 2-butene-1,4-diol (4.28 g., 0.0486 mole) was heated at 80°C. under atmospheric pressure for 48 hr., and under a pressure of 20–25 mm. for 5 hr. more. The polymer obtained was colored dark brown. It was dissolved in acetone, filtered, and evaporated to dryness. A viscous residue remained which solidified to a yellowish powder on standing in a vacuum desiccator over phosphorus pentoxide.

**Polyacetylenedicarboxylate of 2-Butyne-1,4-diol.** This polymer was prepared by several procedures.

(a) A mixture of the diol (4.30 g., 0.05 mole) and of the diacid (5.70 g., 0.05 mole) was heated at 80°C. under atmospheric pressure for 12 hr. The polymer was dissolved in a minimal quantity of acetone. From this solution it was precipitated either by adding chloroform, ethanol or water. The polyester precipitated usually as a viscous oil which solidified in the cold (–20°C.). The light yellow polymer is soluble in acetone, dimethylformamide, dimethyl sulfoxide, and tetrahydrofuran. It softened at about 160–165°C.

(b) 2-Butyne-1,4-diol (0.025 mole) and acetylenedicarboxylic acid (0.025 mole) were dissolved in acetone (20 ml.) and heated in the polymerization vessel at 80°C. under atmospheric pressure. The acetone distilled out, and a viscous liquid remained. The heating was continued for

24 hr. at atmospheric pressure and at 25 mm. for 2.5 hr. further. The polymer was purified as before and had the same properties.

(c) 2-Butyne-1,4-diol (0.05 mole) and acetylene dicarboxylic acid (0.05 mole) were dissolved in acetone (50 ml.) and the solution was refluxed for 24 hr. The solution was transferred to the polymerization vessel and heated at 80°C. The acetone distilled out, and the viscous oily residue was heated for 22 hr. at atmospheric pressure and for a further 4 hr. at 70 mm. The polymer was purified as before. It softened at 150–175°C. It had a carboxyl value of 136.6 mg. NaOH/g. polymer and a hydroxyl value of 100.2 mg. NaOH/g. polymer, which leads to a molecular weight of 338.

ANAL. Calcd. for  $(C_8H_4O_4)_2 + H_2O$ : C, 55.5%; H, 2.9%. Found: C, 54.7%; H, 4.0%.

(d) 2-Butyne 1,4-diol (0.05 mole) and acetylenedicarboxylic acid (0.05 mole) were dissolved in dioxane (50 ml.) and the solution was refluxed for 24 hr. The solution was transferred to the polymerization vessel and heated for 2 hr. at 80°C. and 30 mm. pressure to evaporate the dioxane. The residue was heated at 80°C. under atmospheric pressure for 20 hr. and for a further 4 hr. under 55 mm. pressure. The polymer was purified as before. It softened at 150–175°C. It had a carboxyl value of 92.3 mg. NaOH/g. polymer and a hydroxyl value of 62.0 mg. NaOH/g. polymer, which leads to a molecular weight of 518, equivalent to a trimer.

ANAL. Calcd. for  $(C_8H_4O_4)_3 + H_2O$ : C, 56.4%; H, 2.7%. Found: C, 55.5%; H, 4.0%.

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### Résumé

On a préparé et caractérisé des polyesters acétyléniques contenant soit des résidus de 2-butène-1,4-diol, soit de l'acide acétylène-dicarboxylique ou bien les deux. En employant des méthodes connues, on a obtenu des polymères solubles de polyesters de 2-butène-1,4-diol avec les acides succinique, adipique et phtalique. L'ester polymaléique du 2-butène-1,4-diol a été obtenu soit comme polymère soluble, soit comme polymère insoluble suivant les conditions expérimentales. Une température relativement élevée ou de longues périodes de réaction conduisent à la formation de polymères insolubles. Des polyesters de l'acide acétylène, dicarboxylique avec le diéthylène glycol, les tétra- et hexa-méthylène glycols, le 2-butène-1,4-diol et le 1,4-cyclohexane-diméthylol ont été préparés par polycondensation en bloc à l'état fondu. Ces polyesters sont insolubles, caoutchouteux, exceptés ceux du 2-butène-1,4-diol et du 1,4-cyclohexane-diméthylol, que l'on a obtenu sous forme de polymères linéaires ou non-linéaires. L'insolubilité des polyesters de l'acide acétylène-dicarboxylique est due aux réactions de pontage impliquant le système conjugué  $\text{—C}\equiv\text{C—C=O}$ . Alors que les polycondensations en bloc à l'état fondu comprenant soit le 2-butène-1,4-diol ou l'acide acétylène-dicarboxylique, sont des réactions entièrement contrôlées, celles effectuées entre l'acide acétylène-dicarboxylique et le 2-butène-1,4-diol sont très souvent accompagnées de décompositions fortement exothermiques entraînant une carbonisation. Les décompositions peuvent être éliminées lorsque la polycondensation en bloc à l'état fondu est précédée d'une condensation antérieure en solution. On obtient alors des polymères solides, solubles, pulvérulents, de faible poids moléculaire ( $\text{DP} = 2-3$ ) et possédant des températures de ramollissement d'environ 150–175°C.

### Zusammenfassung

Acetylenpolyester mit 2-Butyn-1,4-diol- oder Acetylendicarbonsäureresten, oder mit beiden, wurden dargestellt und charakterisiert. Polyester von 2-Butyn-1,4-diol mit Bernstein-, Adipin- und Phthalsäure wurden nach bekannten Methoden als lösliche Polymere erhalten. Der Polymaleatester von 2-Butyn-1,4-diol wurde je nach den Versuchsbedingungen entweder als lösliches oder als unlösliches Polymeres erhalten. Relativ hohe Temperaturen oder lange Reaktionszeiten führten zur Bildung unlöslicher Polymerer. Polyester von Acetylendicarbonsäure mit Diäthylenglycol, Tetra- und Hexamethylenglycolen, 2-Buten-1,4-diol sowie 1,4-Cyklohexandimethanol wurden durch Schmelzpolykondensation in Substanz dargestellt. Diese Polyester wurden als unlösliche kautschukartige Stoffe erhalten, mit Ausnahme derjenigen aus 2-Buten-1,4-diol und 1,4-Cyklohexandimethanol, welche sowohl lineare als auch nichtlineare Polymere bildeten. Die Unlöslichkeit der Polyester aus Acetylendicarbonsäure wurde durch Vernetzungsreaktionen mit dem konjugierten System  $\text{—C}\equiv\text{C—C=O}$  verursacht. Während die Schmelzpolykondensation in Substanz mit 2-Butyn-1,4-diol oder Acetylendicarbonsäure vollständig unter Kontrolle gehalten werden konnte, waren die mit Acetylendicarbonsäure und 2-Butyn-1,4-diol ausgeführten oft mit einer hochgradig exothermen Zersetzung mit Karbonisierung verbunden. Die Zersetzung konnte durch Ausführung einer Vorkondensation in Lösung vor der Schmelzpolykondensation in Substanz ausgeschaltet werden. Es wurden so feste, lösliche, pulverartige Niederpolymere ( $\text{DP} = 2-3$ ) mit Erweichungstemperaturen von etwa 150–175° erhalten.

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