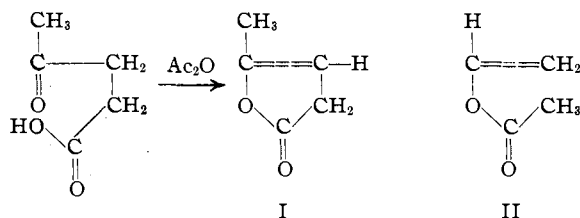


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Structure of Vinyl Polymers. III.<sup>1</sup> The Polymer from  $\alpha$ -Angelica LactoneBY C. S. MARVEL AND CHARLES L. LEVESQUE<sup>2</sup>

$\alpha$ -Angelica lactone (I), readily prepared by the action of acetic anhydride on levulinic acid,<sup>3</sup> may be regarded as a disubstituted vinyl acetate (II)



type. Such esters, with terminal substituents on the vinyl group, do not polymerize readily, but it seemed possible that the strain due to the lactone ring structure might activate the double bond in this case. Although peroxides, the usual catalysts for vinyl polymerization, are ineffective,  $\alpha$ -angelica lactone is easily polymerized by the boron fluoride-ether complex. The product is a tacky, dark red solid. Attempts to remove the color have been unsuccessful.

Long irradiation of  $\alpha$ -angelica lactone with ultraviolet light also produces a polymer. Although less highly colored than the product obtained by the use of boron fluoride, it is also of lower molecular weight, since it shows an appreciable cold flow. Only the polymer formed by the boron fluoride catalyst was used in the investigations reported below.

Cryoscopic determinations in benzophenone and bromine titration of the residual double bonds gave values of 800-900 for the average molecular weight of the polymer. This corresponds to a chain of eight to nine units. The relatively low value of the molecular weight, and the presence of one double bond per molecule indicate a stepwise polymerization related to the Friedel-Crafts reaction, rather than the chain mechanism frequently encountered in other vinyl polymerizations. The double bond is probably in a terminal unit.

Most of the lactone groups are retained in the

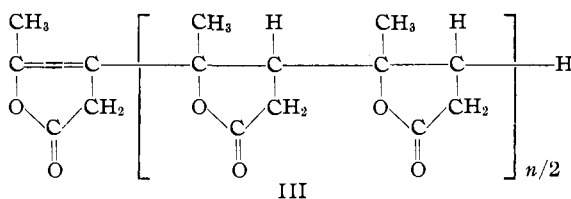
(1) For the second communication in this series, see Marvel and Denoon, *THIS JOURNAL*, **60**, 1045 (1938).

(2) Du Pont Fellow in Chemistry.

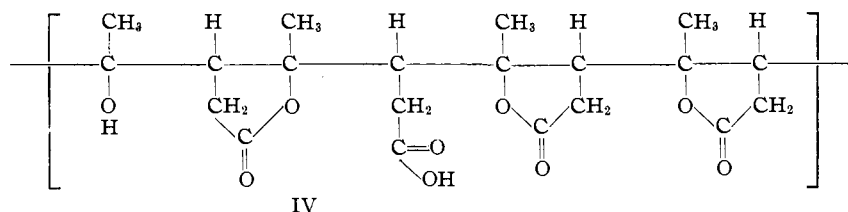
(3) Gilmour, *J. Chem. Soc.*, **105**, 753 (1914).

polymer, since it dissolves only slowly in aqueous sodium hydroxide, reacts with ammonia to produce a poly lactam, and with phenyllithium to give a polyalcohol. As is frequently the case with polymers, the two latter reactions do not proceed to completion. Analysis indicates that in the lactam, 80%, and in the alcohol, 90% of the carbonyl groups have undergone reaction.

Analyses of the original polymer demonstrated that approximately every fourth lactone unit had added a molecule of water. If a "head to tail" structure (III,  $n = 7$  or 8) is assumed for the polymer, this result is readily explained.

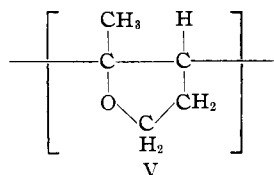


Boron fluoride is a *trans* esterification catalyst, and a *trans* esterification of a polymer such as III would result in the liberation of some hydroxyl and carboxyl groups. Since *trans* esterification is a random reaction certain of these groups will become isolated (IV).



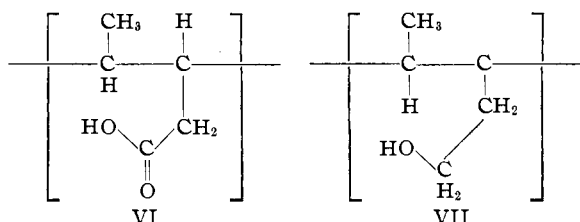
Since this reaction would tend to approach equilibrium, the number of unesterified groups cannot be calculated by Flory's statistical method.<sup>4</sup> The value found, however, is quite consistent with the "head to tail" formulation.

When an attempt was made to hydrogenate the lactone units to tetrahydrofuran units (V) at 250°



(4) Flory, *THIS JOURNAL*, **61**, 1518 (1939).

and 400 atm. over copper-chromium oxide,<sup>5</sup> the amount of hydrogen absorbed was nearly twice that calculated for this reaction alone. The polymeric material isolated weighed only 70% as much as the starting material, and had a much lower average molecular weight. Analysis of this product showed that reactions other than simple hydrogenation of the carbonyl groups had occurred. These facts also pointed to the "head to tail" structure (III), since this structure contains the grouping  $-O-C-C-O$ . It has been shown<sup>6</sup> that in this group, common to 1,3-glycols and their ethers, 1,3-diketones,  $\beta$ -keto esters, etc., the carbon-oxygen bonds and the carbon-carbon bonds are especially sensitive to cleavage by hydrogen at high pressure and temperature over copper-chromium oxide. Under the conditions used in our reduction experiment, in addition to tetrahydrofuran units (V), the polymer III would also produce units of VI and VII,



formed by hydrogenolysis of the carbon-oxygen bond both before and after reduction of the carbonyl group. The analytical results may be explained on the basis that a mixture of these structural units (V, VI and VII) is produced. Hydrogenolysis of the carbon-carbon bonds would account for the lower molecular weight, and the losses.

To test this hypothesis, the original polymer was treated with hydrogen at 175° and 400 atm. over copper-chromium oxide. From certain of the data of Connor and Adkins,<sup>6</sup> it seemed possible that at this temperature, cleavage of the carbon-oxygen bonds might take place to a much greater extent than cleavage of the carbon-carbon bonds. It is obvious that the former cleavage can never be quantitative. In the group

$$\begin{array}{ccccccc} \overset{1}{\text{C}} & - & \overset{2}{\text{C}} & - & \overset{3}{\text{C}} & - & \overset{4}{\text{C}} & - & \overset{5}{\text{C}} & - & \overset{6}{\text{C}} & - & \overset{7}{\text{C}} \\ | & & | & & | & & | & & | & & | & & | \\ \text{O} & & \text{O} & & \text{O} & & \text{O} & & \text{O} & & & & \end{array}$$

for example, cleavage of the bonds, as indicated at carbon atoms 1 and 5, would destroy the 1,3-glycol character of the carbon-oxygen bond at carbon atom 3. Hence

(5) Connor, Folkers and Adkins, *THIS JOURNAL*, **54**, 1138 (1932).  
 (6) Connor and Adkins, *ibid.*, **54**, 4678 (1932).

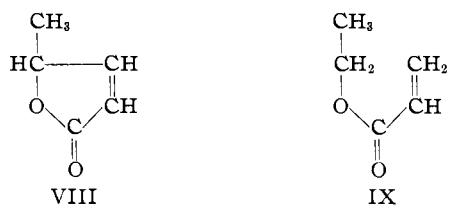
this bond would not cleave. Applying the methods of Flory,<sup>4</sup> and assuming no carbon-carbon cleavage, it may be calculated that for a 1,3-type polymer of  $n$  units, the following relation holds

$$S_n = \frac{2}{n} \left( 1 + \frac{3}{3} + \frac{4}{3} + \frac{5}{3} + \dots + \frac{n}{3} \right) = \frac{n+1}{3}$$

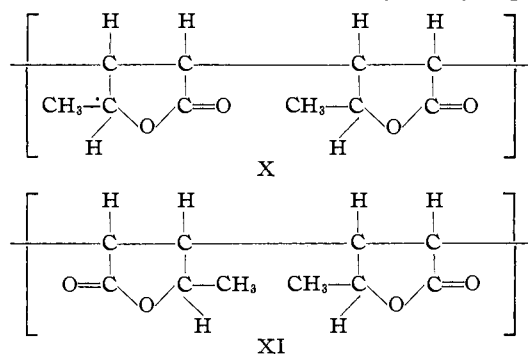
$S_n$  is the number of carbon-oxygen bonds per molecule not cleaved. For an octamer  $S_8 = 3$ . Hence only 62.5% of the carbon-oxygen bonds should be cleaved, and the polymer will take up 0.625 molecule of hydrogen per unit. Since there is also one double bond for every eight units, another 0.125 molecule of hydrogen per unit will be taken up, making the total amount of hydrogen absorbed 0.75 molecule per unit.

This figure agrees satisfactorily with the experimental result. The polymer absorbed  $0.84 \pm 0.05$  molecule of hydrogen per unit to give a quantitative yield of a polyacid. The analysis of the material obtained agreed with that calculated on the assumptions above, and a determination of the molecular weight showed that little carbon-carbon cleavage had taken place.

We have considered the possibility that isomerization of the  $\alpha$ -form to  $\beta$ -angelica lactone (VIII)<sup>7</sup> might have taken place before polymerization. This  $\beta$ -lactone is a substituted ethyl acrylate (IX) type. However, neither of the two



possible structures for a  $\beta$ -angelica lactone polymer (X, XI) would have the 1,3-glycol grouping



which has been shown to be present in our polymer.

(7) Thiele, Tischbein and Lossow, *Ann.*, **319**, 188 (1901); Auwers, *Ber.*, **56**, 1672 (1923).

From these data, the polymer produced from  $\alpha$ -angelica lactone is a polylactone having a "head to tail" structure, and containing about 25% free carboxyl and hydroxyl groups (IV).

### Experimental

**Polymerization of  $\alpha$ -Angelica Lactone by the Boron Fluoride-Ether Complex.**—To a solution of 15 g. of  $\alpha$ -angelica lactone<sup>3</sup> in 40 cc. of carbon disulfide was added 0.4 cc. of the boron fluoride-ether complex. The solution was refluxed gently for five hours. The colorless supernatant layer was decanted from the viscous red polymer layer which was then washed by decantation with several portions of ether, and freed of volatile matter by heating slowly (one and a half hours) to 80° at 2 mm. There remained 14.7 g. of a dark red solid, tacky, but showing no cold flow. It was readily soluble in acetone, dioxane, cellosolve, ethyl alcohol and butyl alcohol, slowly soluble in aqueous sodium hydroxide, insoluble in water, ether, benzene and ligroin.

Mol. wt. (benzophenone): 845. Bromine titration: 3.030 g. of polymer in ethanol-chloroform required 17.3 cc. of 0.214 *N* bromine in carbon tetrachloride; eq. wt., 818. The polymer may also be prepared in ether solution, though in lower yields.

*Anal.* Calcd. for  $(C_8H_8O_2)_4 \cdot H_2O$ : C, 58.4; H, 6.40. Found: C, 58.17, 58.19, 58.38; H, 6.64, 6.89, 6.56.

**Polymerization of  $\alpha$ -Angelica Lactone by Ultraviolet Light.**—Five cubic centimeters of  $\alpha$ -angelica lactone in a quartz test-tube was irradiated for two weeks with light from a mercury vapor arc. At the end of this time, the lactone had polymerized to a very viscous orange liquid. The liquid had the same solubility characteristics as the boron fluoride catalyzed polymer.

**Poly- $\alpha$ -angelica Lactam.**—A solution of 6.0 g. of polylactone in 50 cc. of dioxane was placed in a glass-lined steel bomb, cooled in dry-ice, and 20 cc. of liquid ammonia added. The bomb was sealed, and heated at 150–160° for three hours, then allowed to cool to room temperature overnight. The glass liner containing the reaction mixture was removed, the supernatant liquid decanted and the precipitated polymer washed with dioxane and ligroin. After drying *in vacuo* over concentrated sulfuric acid 4.0 g. of brittle, red-brown solid remained. It was readily soluble in water.

*Anal.* Found: N, 11.59.

Assuming the free carboxyl groups (IV) are converted to ammonium salt groups, this analysis shows that 84% of the lactone groups have been converted to lactam groups.

**Reaction of Polylactone with Phenyllithium.**—A solution of phenyllithium in ether was prepared under nitrogen from 2.3 g. of lithium and 25 g. of bromobenzene, and the ether displaced by toluene. To this was added a solution of 6.0 g. of the polylactone in a mixture of 50 cc. of dimethyl ether of ethylene glycol and 50 cc. of toluene.

Heat was evolved and a reddish-brown, flocculent precipitate formed. The mixture was stirred and heated on a steam cone for sixteen hours then 50 cc. of water was added cautiously and steam passed through the mixture for two hours to remove solvents and diphenyl. Fifteen cubic centimeters of concentrated hydrochloric acid was added, and the steam distillation continued for one hour. The hot polymer, which had collected as a heavy, oily liquid, was thoroughly washed with several portions of hot water. After cooling, and drying *in vacuo* over sulfuric acid, 10.0 g. of plastic, chocolate brown solid remained. It was soluble in alcohol, and insoluble in aqueous sodium hydroxide.

*Anal.* Calcd. for  $C_{17}H_{18}O_2$ : C, 80.2; H, 7.14. Found: C, 78.15; H, 6.85.

**Hydrogenation of the Polymer at 250°.**—A solution of 10 g. of the polylactone in 135 cc. of butanol was twice refluxed over Raney nickel, and filtered into a 280-cc. steel bomb. Five grams of copper-chromium oxide catalyst<sup>5</sup> was added and the bomb filled with hydrogen at 3325 lb. (222 atm.) and 25°. After shaking at 250° for ten and a half hours, the pressure drop (after cooling) was 900 = 20 pounds, equivalent to 3.92 = 0.05 moles of hydrogen per mole of polymer unit. The reaction mixture was filtered, centrifuged, and the solvent removed *in vacuo* in a stream of nitrogen. The residual liquid was washed into an evaporating dish with a little alcohol and, after drying *in vacuo* over sulfuric acid, left 7 g. of a light brown, viscous liquid.

*Anal.* Calcd. for  $C_8H_8O$ : C, 71.5; H, 9.6;  $C_8H_{10}O$ : C, 69.8; H, 11.8;  $C_8H_8O_2$ : C, 60.0; H, 8.06. Found: C, 67.54; H, 9.94; mol. wt. (benzophenone), 351.

**Hydrogenation of the Polylactone at 175°.**—Fourteen and eight-tenths grams of polymer was dissolved in 140 cc. of dioxane which previously had been treated with hydrogen and copper-chromium oxide. The solution was twice refluxed over Raney nickel and then filtered into a 280-cc. steel bomb containing 5.0 g. of copper-chromium oxide. Hydrogen at 4100 lb. (273 atm.) and 25° was admitted and the bomb shaken at 175° until absorption of hydrogen ceased (twenty hours). The pressure drop (cold) was 320 = 20 pounds, equivalent to 0.84 = 0.05 mole of hydrogen per mole of polymer unit. The product was isolated as before, giving 15.1 g. of a very viscous brown polymer, insoluble in water, but readily soluble in aqueous sodium bicarbonate.

*Anal.* Calcd. for 75%  $C_8H_8O_2$  + 25%  $C_8H_8O$ : C, 60.31; H, 7.58. Found: C, 60.20; H, 7.24; mol. wt. (benzophenone), 767.

### Summary

The polymer prepared by the action of boron fluoride-ether complex on  $\alpha$ -angelica lactone has been shown to be a polylactone having the "head to tail" structure.

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