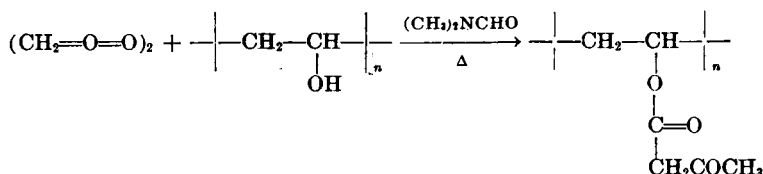


## Polymeric Ligands IV.<sup>1</sup> Polyvinyl $\beta$ -ketoesters

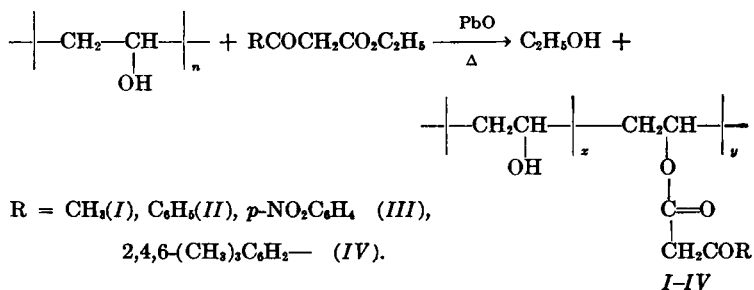
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### RESULTS AND DISCUSSION

The preparation of polyvinyl acetoacetate has been reported by Staudinger<sup>2</sup> and others.<sup>3</sup>

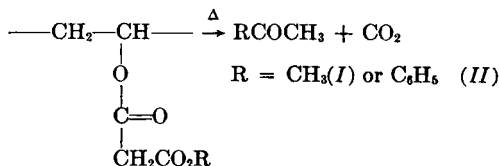


To our knowledge, the preparation of other polymers of this type has not been reported. We have found that copolymers of vinyl alcohol and vinyl acetoacetate can be prepared by ester interchange of the appropriate  $\beta$ -ketoester with polyvinylalcohol.



The polymers which were prepared in the fashion described above were spongy, insoluble yellow solids which had infrared spectra consistent with the assigned structures and which appeared to be crosslinked. Where no catalyst or nonmetallic catalysts were used, soluble products were obtained. All the products were copolymers except IV. This product was a homopolymer. All the polymers formed a red iron chelate when contacted with iron III. The polymers could be used as chelate ion exchangers. Such chelates were prepared by stirring the polymers in aqueous solutions of Th<sup>IV</sup>, Ce<sup>III</sup>, La<sup>III</sup>, UO<sub>2</sub><sup>+2</sup>, Al<sup>III</sup>, and Cu<sup>II</sup>.

The first polymers prepared were *I* and *II*. The elemental analyses of these products made it clear that copolymers not homopolymers were formed. In order to get some idea of the number of  $\beta$ -ketoester units present in the average molecule, the polymers were pyrolyzed.



It is known that the pyrolysis of ethyl acetoacetates yields similar results.<sup>4</sup>



Pyrolysis of *I* showed that a minimum of 36.4% of the alcohol groups in the polymer were converted to  $\beta$ -ketoester groups. Similarly, pyrolysis of *II* showed that the copolymer contained a minimum of 73% of  $\beta$ -ketoester groups. Nitrogen analysis of *III* indicated a ratio of 8 polyvinylalcohol mers/1 ester mer present in the copolymer and elemental analysis of *IV* showed that the product was a homopolymer.

*II* could be pressed into rigid transparent films at 70–80° and 5–10,000 p.s.i. on a Carver press. Pressing at 150–180° gave opaque flexible films. The other polymers could not be pressed into films under similar conditions.

## EXPERIMENTAL

### *Preparation of Vinyl Acetoacetate-Vinyl Alcohol Copolymers*

A mixture of 490 g. (3.8 mole) of ethyl acetoacetate, 88 g. (2 mer moles) of polyvinylalcohol (Elvanol 72–51) and 10 g. of litharge was stirred vigorously at 140–160° in an oil bath with good agitation until 120 ml. of distillate was collected. The distillate was largely ethanol contaminated with methanol, ethyl acetate, and acetone. The ethanol was identified by gas chromatography and by the preparation of classical derivatives. The reaction mixture was cooled, hexane added to the mixture, and the product removed by filtration. The crude product was extracted overnight with water in a Soxhlet extractor and then extracted overnight with acetone. The product was dried under vacuum and pulverized at dry ice-acetone temperatures in a micropulverizer to yield a fine water-swellaible powder. The yield was 122 g.

### **Characterization of Vinyl Acetoacetate-Vinyl Alcohol Copolymers**

The resin preparation which was described in the preceding section gave a product with an infrared spectrum which might be expected from such a polymeric structure. The carbon hydrogen analysis was not definitive. However, by pyrolysis of the resin the structure of the polymer was definitely established.

One hundred two and five-tenths grams of the resin was pyrolyzed in a round-bottom flask with a free flame until no more gas was evolved and destruction of the resin was complete. The pyrolysis gases were passed through a water condenser, a distillate receiver, two cold traps, and then two gas traps filled with 10% sodium hydroxide. The entire pyrolysis system was kept under a slight positive pressure of nitrogen. The organic material of the distillate and the cold traps was separated from the water by chloroform extraction. The chloroform extract was analyzed for acetone. It contained 21.14 g. of acetone by vapor fractometer analysis. Therefore, 36.4% of the hydroxyl groups in the polyvinylalcohol were esterified to yield polyvinyl acetoacetate mers. The sodium hydroxide wash solutions were treated with a freshly prepared solution of barium hydroxide. Barium carbonate was precipitated to confirm the presence of carbon dioxide in the off-gas of the pyrolysis.

### **Preparation and Characterization of Vinyl Benzoylacetate-Vinyl Alcohol Copolymers**

A mixture of 44 g. (1 mer mole) of 70% hydrolyzed vinyl alcohol-vinylacetate copolymer (Elvanol 32A-70) having a viscosity of 70 cp., 200 g. (1.04 mole) of ethyl benzoylacetate, and 5 g. of litharge was heated with strong stirring until 20 ml. of ethanol distilled over. The product was extracted continuously for 48 hrs. with boiling water and then for 48 hrs. with acetone. The product was ground on a micropulverizer at dry-ice acetone temperatures to yield 73.7 g. of material the infrared spectrum of which was consistent with the structure of the expected product. When 50 g. of the product was pyrolyzed in a fashion identical to the pyrolysis of the polyvinylacetoacetate-polyvinylalcohol copolymers previously described, 15.8 g. of acetophenone was isolated which indicated that a minimum of 73% of polyvinylbenzoylacetate groups were present in the polymer. The trapped off-gas again yielded barium carbonate on treatment with barium hydroxide solution.

### **Preparation of Soluble Vinyl Alcohol-Vinyl Benzoylacetate Copolymers**

(A) Forty-four grams (1.0 mer mole) of polyvinylalcohol (Elvanol 32A-70) was mixed with 200 g. (1.04 mole) of ethyl benzoylacetate. The mixture was heated in a 500 ml. three-necked flask equipped with a mechanical stirrer, thermometer, and a condenser. The mixture was heated at 150–170° in an oil bath until 18 ml. of distillate was collected. The gel which formed was extracted overnight in a Soxhlet extractor with ethanol and then for 24 hrs. with water, and for 24 hrs. with acetone, dried, and ground in a Waring blender. The product was soluble in dimethylformamide. This polymer could be pressed into tough yellow transparent films on a Carver press at 70–80° and 5–10,000 p.s.i. When films were pressed at 150–180° under otherwise identical conditions, soft opaque films were formed.

(B) A mixture of 11 g. (0.2 mole) 70% hydrolyzed polyvinyl alcohol, 100 g. (0.52 mole) ethyl benzoylacetate, and 0.3 g. (0.001 mole) iodine was placed in a 500 ml. three-necked flask with a mechanical stirrer and a thermometer. The temperature of the mixture was maintained at 125° for six hours; the mixture becoming a brown gummy mass. A solution of 200 ml. acetone, 30 ml. water and 3 g. (0.018 mole) sodium thiosulfate pentahydrate was added to the cooled gummy mass, and the entire solution stirred for two days. The product was precipitated from acetone with diethyl ether three times. The clear light tan thermoplastic (softening point = 60°) was obtained in 75% yield, and was soluble in acetone, and dimethyl formamide.

#### Preparation of Vinyl Alcohol-Vinyl-4-Nitrobenzoylacetate Copolymer

A mixture of 4.4 g. (0.1 mer mole) of polyvinylalcohol (Elvanol 72-51) and 47.4 g. (0.2 mole) of ethyl 4-nitrobenzoylacetate,<sup>5</sup> and 0.5 g. of litharge was heated with strong stirring until 4 ml. of distillate was collected. The product was removed from the flask by rinsing with acetone or petroleum ether and placed in the cup of a Soxhlet extractor. The product was extracted for 8 hrs. with water and overnight with acetone. The product was dried and pulverized in a Waring blender.

ANAL.: Calculated for  $C_{27}H_{41}O_{11}N$ : N, 2.38%; found: 2.38%, 2.24%.

#### Preparation of Polyvinyl 2,4,6-Trimethylbenzoylacetate

A mixture of 2.2 g. (0.05 mer mole) of polyvinyl alcohol (Elvanol (72-51), 23.4 g. (0.1 mole) of ethyl 2,4,6-trimethylbenzoylacetate,<sup>6</sup> and 0.5 g. of litharge were mixed and heated with good agitation until 3 ml. of distillate

TABLE I  
Capacity of Polymer I for Various Metal Ions

Metal ion	pH	Capacity (meq./g. I)
La <sup>III</sup>	1	0.02
La <sup>III</sup>	2	0.03
La <sup>III</sup>	3	0.10
La <sup>III</sup>	4	0.24
Ce <sup>III</sup>	1	0.30
Ce <sup>III</sup>	3	0.36
Ce <sup>III</sup>	4	0.39
Th <sup>IV</sup>	1	0.11
Th <sup>IV</sup>	2	0.49
Th <sup>IV</sup>	3	0.49
UO <sub>2</sub> <sup>+2</sup>	1	0.09
UO <sub>2</sub> <sup>+2</sup>	2	0.21
UO <sub>2</sub> <sup>+2</sup>	3	0.51
Al <sup>III</sup>	1	0.10
Al <sup>III</sup>	2	0.10
Cu <sup>II</sup>	1	0.05
Cu <sup>II</sup>	2	0.08
Cu <sup>II</sup>	4	0.32

was collected. The product gel was extracted for 8 hrs. in a Soxhlet extractor with water and overnight with acetone. The dried product was ground in a Waring blender.

ANAL.: Calculated for  $C_{14}H_{16}O_8$ : C, 72.4%; H, 6.93%; found: C, 72.6%; H, 7.52%.

### Chelate Ion Exchange Experiments with a Vinyl Alcohol-Vinyl Acetoacetate Copolymer (I)

When the polymer (I) was stirred with 0.1 *M* solutions of various metal ions at constant pH until equilibrium was reached, the polymer had the working capacities shown in Table I. The metal ions could be eluted from the polymer with acid and the polymer reused.

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### Synopsis

Copolymers were prepared by ester interchange of polyvinylalcohol with ethyl acetoacetate, ethyl benzoylacetate, and ethyl 4-nitrobenzoylacetate. Reaction of ethyl 2,4,6-trimethylbenzoylacetate with polyvinylalcohol yielded a homopolymer. The polymers functioned as chelate ion exchangers. Ion exchange capacities were determined for the polymer derived from polyvinylalcohol and ethyl acetoacetate.

### Résumé

On a préparé des copolymères par estérification de l'alcool polyvinylique avec l'acétoacétate d'éthyle, le benzoylacétate d'éthyle et le 4-nitrobenzoylacétate d'éthyle. On a obtenu un homopolymère par réaction du 2,4,6-triméthylbenzoylacétate d'éthyle avec l'alcool polyvinylique. Les polymères agissent comme chélates, échangeurs d'ions. On a établi les capacités d'échangeurs d'ions pour les polymères dérivés de l'alcool polyvinylique et de l'acétoacétate d'éthyle.

### Zusammenfassung

Copolymere wurden durch Umesterung von Acetessigester, Benzoylessigsäureäthylester und 4-Nitrobenzoylessigsäureäthylester mit Polyvinylalkohol dargestellt. Die Reaktion von 2,4,6-Trimethylbenzoylessigsäureäthylester mit Polyvinylalkohol lieferte ein Homopolymeres. Die Polymeren bildeten Chelat-Ionenaustauscher. Die Austauschkapazität des Polymeren aus Polyvinylalkohol und Athylacetoacetat wurde bestimmt.

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