A STUDY OF THE SYNTHESIS

OF POLYVINYL ALCOHOL

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TABLE OF CONTENTS

INFRARED SPECTRUM CHARTS

TABLES OF INFRARED ABSORBANCES

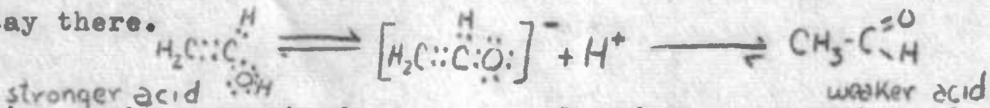
Introduction:

Polyvinyl alcohol is a high molecular weight polymer whose repeating unit is $-(-CH_2-CHOH-)_n$. From this the expected monomer from which polyvinyl alcohol would be produced is vinyl alcohol, $CH_2=CHOH$, however, vinyl alcohol does not exist in the free state, for it is very unstable in nature.

Apparently, all reactions which would yield vinyl alcohol undergo a rearrangement to the more stable acetaldehyde or keto form. This is caused by the desire to relieve the strain of the double bond in vinyl alcohol.[1]

$$CH_3C(=O)-O-CH=CH_2 \xrightarrow{HOH} CH_3C(=O)OH + [CH_2=C(H)OH] \rightleftharpoons CH_3C(=O)H$$

Rearrangements of this enol-keto type take place particularly easily because of the polarity of the --O-H bond and the very high electron density that attempts to become more stable by shifting a hydrogen. To relieve this strain, a hydrogen ion separates readily from oxygen, but when a hydrogen ion (most likely a different one) returns it may attach itself either to oxygen or to carbon. If it returns to oxygen, it may readily come off again; but if it attaches itself to carbon it tends to stay there.



This can be recognized as an example of the conversion of stronger acid into a weaker acid.[2]

Acetaldehyde has been polymerized to rubber-like soluble products. The failure of these products to readily acetylate, together with their lack of water solubility, show them to be of a different structure than true polyvinyl alcohols. However, it should theoretically be possible to prepare polyvinyl alcohol by the appropriate polymerization of acetaldehyde.[3]

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1. C.E. Schildknecht, Vinyl and Related Polymers, (John Wiley & Sons Inc., New York 1953)
2. R.T. Morrison and R.N. Boyd, Organic Chemistry, (Allyn & Bacon Inc., Boston 1959), p. 174
3. Jack Dickstein and Robert Bouchard, Manufacture of Plastics, (Rheinhold Publishing Co. 1964), p. 256

As can readily be deduced from the foregoing discussion, the synthesis of polyvinyl alcohol must proceed through an alternate route. The most common procedure begins with vinyl acetate which is polymerized to polyvinyl acetate and subsequently hydrolyzed to polyvinyl alcohol.

Preliminary solubility tests were run in order to find an appropriate solvent for the hydrolysis reaction. It was found that polyvinyl alcohol is soluble in water to the extent of approximately five to six grams per one hundred milliliters. As verified by a literature search it was found that polyvinyl alcohols are used as tubing in which organic materials are transported; therefore, polyvinyl alcohol is not soluble in organic solvents. Several organic solvents were tested including the butyl alcohols, benzene, methanol and acetone. In methanol it is approximately soluble to the extent of two tenths of a gram per one hundred milliliters.

It was also found in a literature search that polyvinyl acetate is soluble in methanol to the extent of five grams per one hundred milliliters. Therefore, methanol was chosen as the solvent. The hydrolysis reaction would tend toward completion because the product, polyvinyl alcohol, would precipitate from the solution as the reaction progresses.

The Monomer Vinyl Acetate

Vinyl acetate is of the vinyl family whose general formula is $CH_2=CXY$. In this case X is equal to a hydrogen and Y equals the acetate group, CH_3COO--. Vinyl polymers are the most common addition-type polymer which are formed by the addition of one monomer molecule to another without loss of any portion of the monomer. Long chains develop whose general repeating unit is $-\!(\!-CH_2-CXY-\!)\!-_n$. There are three general mechanisms by which vinyl monomers may polymerize, and each depends upon the initiator used to begin the reaction.

The first is the free radical mechanism which is started by a molecule that is electron deficient of having a stable octet by one. This molecule begins the reaction by attacking the carbon-carbon double bond of the monomer in order to gain the electron it needs. As a result it leaves the vinyl monomer to which it is attached electron deficient by one. This new free radical may similiarly attack another monomer molecule and so on until a long chain grows.

Cationic initiators are positively charged and are seeking a pair of electrons for a stable octet. These electrons may be found at the carbon double bond site. When this initiator attaches itself to the monomer, it leaves the monomer electron deficient by two. Again by the same mechanism this positively charged aggregate may further attack another molecule of monomer until finally long chains develop.

Sometimes even anionic or nucleophilic initiators may be used. Since they are electron rich and seek a positive charge, they can only be used if the substituents, X and Y, of the vinyl monomer deactivate the double bond[4] by delocalizing the electrons. Once initiated the reaction proceeds as mentioned above except a negatively charged species does the attacking.

Since vinyl monomers are so reactive, they may be initiated by impurities within them, and therefore inhibitors are placed in them for storage. This inhibitor must be removed in order

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4. Patrick Meares, <u>Polymers: Structure and Bulk Properties</u>, (D. Van Nostrand Co., New York 1965) p.8

that polymerization may take place. Since vinyl acetate is highly inflammable, distillation to remove the inhibitor was carried out solely by reduced pressure.

An infrared spectrum of the purified vinyl acetate monomer was taken using a potassium bromide liquid cell. This spectrum appears below and will be compared with the spectra of polyvinyl acetate and polyvinyl alcohol.

Peaks of the Vinyl Acetate Spectrum[5]

cm^{-1} of band	absorbing group
3095 - 3075	C-H stretching of a monosubstituted vinyl group.
1730 - 1715	C=O stretching vibrations of an alpha:Beta unsaturated ester.
1645 - 1640	C=C stretching vibrations of monosubstituted alkenes.
1360 - 1355	CH_3 deformation of the CH_3-CO- group.
1220 - 1200	C-O stretching vibration due to vinylic acetates.

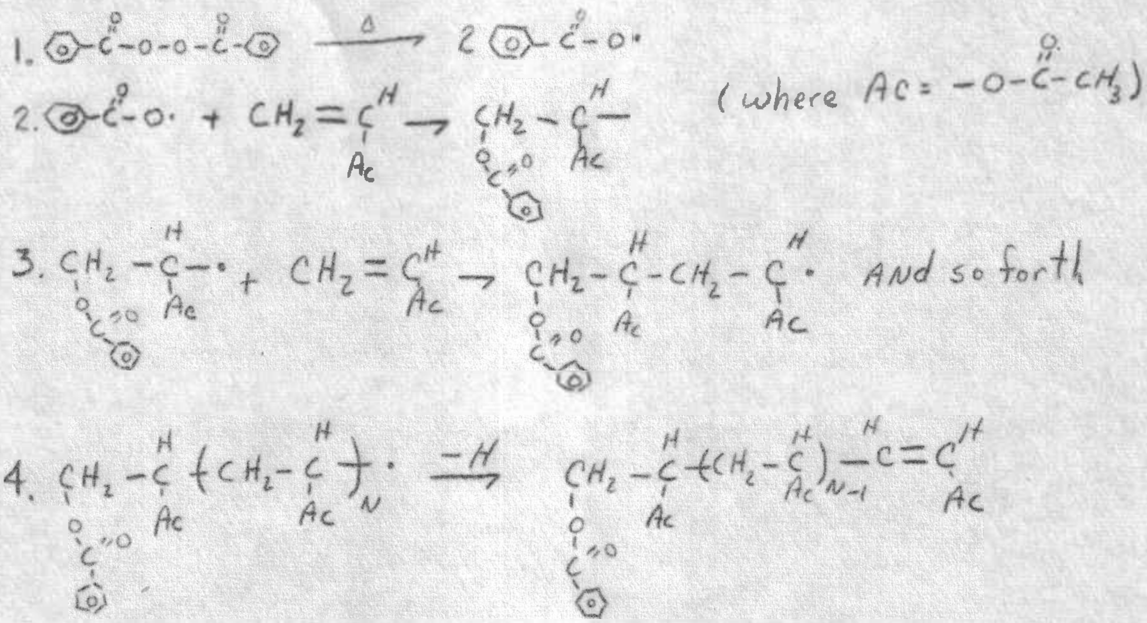
5. A.D. Cross, Introduction to Practical Infra-red Spectroscopy, (Butterworth & Co., London 1964) p. 63 - 70

The Free Radical Initiator

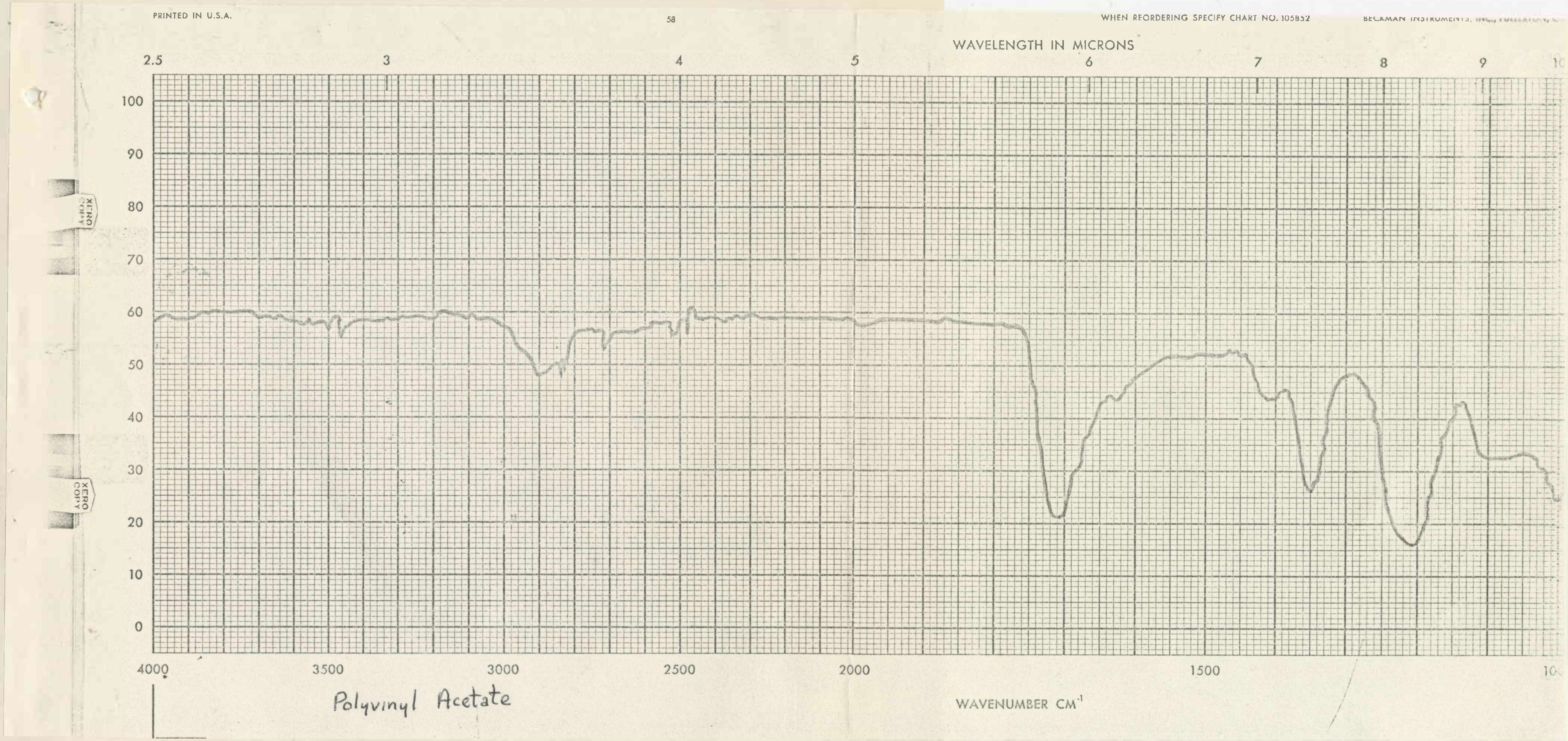
The initiator used in the free radical polymerization was benzoyl peroxide of which one hundredth of a gram was dissolved in fifty milliliters of vinyl acetate. The resulting solution was refluxed for three hours. The solution became increasingly viscous and finally a gummy, clear solid formed. The polyvinyl acetate produced was dissolved in five hundred milliliters of methanol and brought to a gentle boil under reflux. Five per cent sodium methoxide in methyl alcohol was added to the refluxing polymer solution in five to ten milliliter portions at intervals of five minutes.[6]

Almost immediately upon the addition of the methoxide solution, polyvinyl alcohol precipitated from the solution in small, white, crystal-like globules. The polymer was collected on a Buchner funnel with gentle suction and washed with methanol. The product was a white gelatine-like substance which was placed in a desiccator to dry.

The mechanism of the reaction is as follows:



6. Dickstein and Bouchard, p. 257



The spectra of polyvinyl acetate appears above. When it is compared to that of its monomer vinyl acetate, certain differences are able to be noted in the disappearance of two major identifiable peaks. These peaks are present on the monomer spectra, but they do not appear on the polymer spectra. First of all, the peak at 3090 reciprocal centimeters is due to the C-H bond stretching and deformation vibrations of a monosubstituted vinyl group, and the peak at 1645 reciprocal centimeters is due to carbon-carbon multiple bond stretching of a monosubstituted alkene.

A third peak which is at 3500 cm^{-1} also disappears, but it was not able to be accurately identified.

The disappearance of these peaks in the polymer spectrum is to be expected since the only double bonds possible are those which are formed in chain terminations. These are so few that they cannot be detected.

A peak appears on the polymer spectrum that does not appear on the spectrum of the monomer. At 2940 to 2915 cm^{-1} the absorption band due to $--CH_2--$ stretching is present on the spectrum of polyvinyl acetate.

The spectrum of polyvinyl alcohol produced by the transesterification of polyvinyl acetate is given on the following page. A chart of the major identifiable absorbance bands is given below.

Absorbance Bands of Polyvinyl Alcohol[7]

Cm^{-1} of band	Absorbing group
3400 - 3200	O-H stretching vibrations of polymeric association.
2940 - 2915	$--CH_2--$ stretching vibrations.
1485 - 1445	$--CH_2--$ bending vibrations.
1350 - 1260	C-O bending vibrations of secondary alcohols.
1120 - 1030	C-O stretching vibrations of secondary alcohols.

A comparison of the polyvinyl alcohol spectrum to that of polyvinyl acetate shows immediately that different absorbing groups are present. The peaks due to the absorbance of the acetate group have been replaced by peaks assigned to the secondary alcohol functional group.

7. Cross, p.63 - 70

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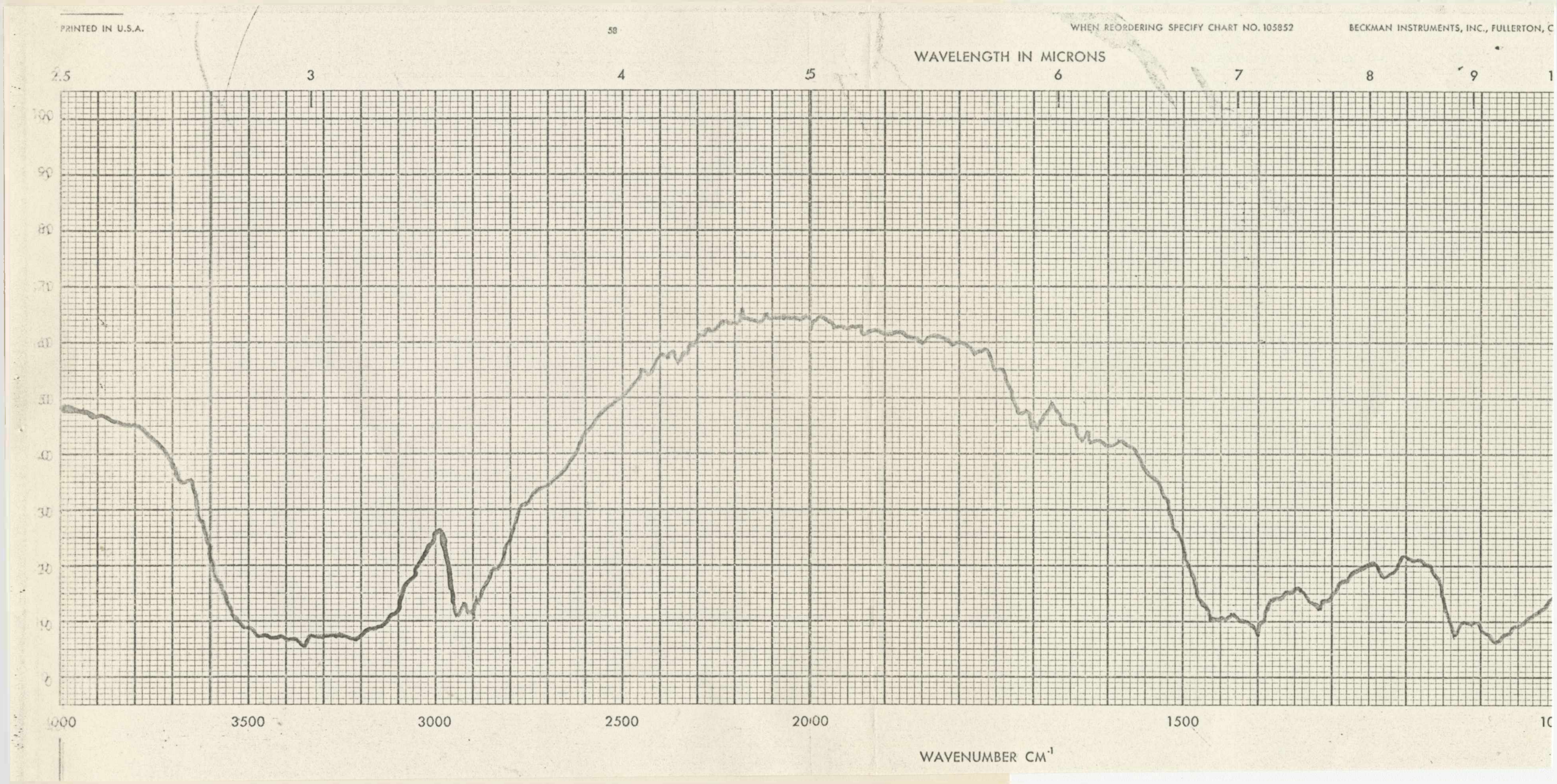
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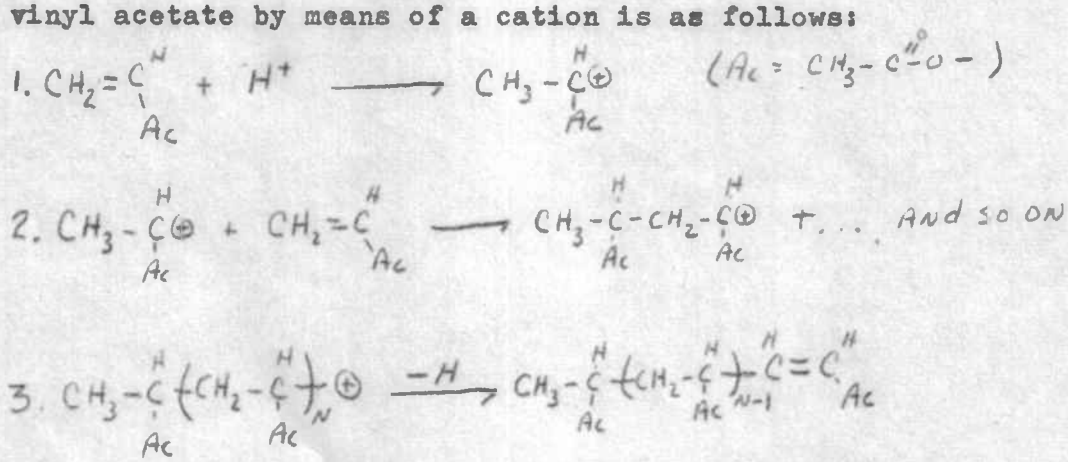
Cationic Initiator

Several attempts were made to polymerize vinyl acetate with cationic initiators. All of these attempts proved to be rather unsuccessful because they produced large amounts of unidentifiable decomposition products. The formation of these decomposition products in addition to the relative speed of the reaction seem to indicate that the carbon-carbon double bond of vinyl acetate is highly vulnerable to cationic attack.

The general reaction mechanism of the polymerization of vinyl acetate by means of a cation is as follows:



Dilute sulfuric acid attacked the monomer with such violence, even when the reaction solution was cooled in an ice bath, that great amounts of black decomposition product resulted. Only small amounts of polymer were obtained and these were always slimy masses that were only partially soluble in methanol and that were very difficult to collect. For these reasons, no attempt was made to further react the product obtained into polyvinyl alcohol.

Two Lewis acids were used as initiators, boron trifluoride and aluminum chloride. The most successful was boron trifluoride in complex with ethyl ether. This completely polymerized the vinyl acetate under reflux in approximately ten to twelve minutes, however the polyvinyl acetate obtained by this reaction contained a large amount of decomposition products. In an attempt to produce the polymer without the decomposition, the reaction was carried out in an ice bath. No visible reaction could be detected, so the solution was heated very gently until a slight discoloration was observed then the reaction vessel was placed back into the ice bath. The reaction seemed to stop, for there was not any increase in the solution viscosity even after three hours. The solution was allowed to stand at room temperature over night with the result that became much more viscous, but black in color due to the presence of decomposition products.

Because of the large amounts of unidentifiable decomposition products that turned the polymer black and for all practical purposes opaque to infrared, no spectra of the polymer formed by cationic initiators could be made.

Anionic Initiator

Attempts to initiate the polymerization with a nucleophile were unsuccessful. Two trials were made;one using the Grignard reagent and the other using phenyl sodium.

The phenyl sodium was produced by adding finely divided sodium metal to refluxing benzene. When a small amount of the phenyl sodium was added to the monomer and allowed to reflux for four hours, seemingly no reaction had taken place. The solution appeared to just as viscous after the refluxing as it was before the initiators were added.

A second attempt by an anionic initiator used the Grignard reagent. Phenyl magnesium bromide was added to the monomer and a white precipitate formed in a yellow solution immediately upon the addition. This solution was refluxed for four hours, allowed to stand overnight, and refluxed for an additional two hours. The resulting solution was separated from the precipitate by means of water in a separatory funnel. After the separation the yellow solution was refluxed for three hours. Several drops were placed on a potassium bromide pellet and an infrared spectrum made. The spectrum obtained did not contain any identifiable peaks and was useless for structure determination. Most likely the Grignard reagent found a more reactive site at the carbonyl of the acetate group and therefore polymerization did not occur.

Conclusion

From the foregoing it can be said that the carbon-carbon double bond electrons of vinyl acetate are rather available at the double bond site. The acetate group does not deactivate the double bond, for the free radical reactions proceeded with relative ease, and from all appearances the anionic initiator cannot react at the double bond. In fact, as shown by the reaction of the cationic initiators, the acetate group may make the electron cloud of the double bond more dense. However, due to a lack of time the appropriate conditions for a cationic polymerization were not able to be found.

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