# Preparation of Copoly(vinyl alcohol—styrenesulfonic acid) Resin and Its Catalytic Activity on Hydrolysis of Carbohydrates

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ABSTRACT: A ternary suspension copolymerization of vinyl acetate, styrene, and divinyl benzene was carried out, and changes in the yield of the insoluble copolymer and weight per cent of vinyl acetate unit in the copolymer obtained were investigated with changing reaction time and composition of the monomer mixture. This copolymer of white granules ranging from 0.45—0.55 mm in diameter was sulfonated with sulfur trioxide gas, saponified with sodium hydroxide in methanol and then washed with hydrochloric acid to obtain a free-acid-type catalyst. The hydrolysis of dextrin in the presence of the catalyst was investigated. The catalytic activity was found to increase with increasing amounts of hydroxyl group in the copolymer, and rate enhancements of up to nine fold were found relative to the reaction in the presence of the catalyst containing no hydroxyl group.

KEY WORDS    Ternary Suspension Copolymerization / Polymer Catalyst / Hydrolysis of Carbohydrates / Heterogeneous Catalyst / Substrate Binding Effect /

Generally, a heterogeneous catalysis is advantageous from standpoint of product isolation and regeneration of the catalyst, although heterogeneous catalysts usually have activities lower than their homogeneous counterparts for the same reaction. In order to utilize such advantages, the fixation of enzyme, for example, the subject of numerous investigations.[1] Some attempts have also been made to bring about the hydrolysis of carbohydrates. For example, Hartler, *et al.*,[2] found that in the hydrolysis reaction of sucrose, catalyzed by a poly(styrenesulfonic acid)-type cation exchanger, the reaction rate was 1.25 times higher than that in the reaction catalyzed by sulfuric acid, and that in the case of cotton, the reaction did not proceed practically. These reactions can be expected to accelerate by the introduction of functional groups, which may interact with the substrates, to the catalyst; in homogeneous systems, hydrolysis of dextrin has been found to be accelerated by the introduction of hydroxyl groups to the poly(vinylsulfonic acid) which is the catalyst for the reaction.[3] In

a previous work,[4] the catalytic activity of poly-(vinyl alcohol)-grafted ion exchangers on hydrolysis of dextrin was investigated, and a tendency for the activity to increase with an increasing graft ratio was found. However, the maximum acceleration of the reaction was 1.5 times that in the presence of the original resin because of the limited ratio.

In the present experiment, in order to obtain similar copolymers containing more vinyl alcohol sequence, a ternary suspension copolymerization of vinly acetate, styrene and divinyl benzene was examined. The crosslinked copolymer obtained was sulfonated, saponified, and washed with hydrochloric acid in order to obtain a free-acid-type catalyst. The catalytic activity of the copolymer catalyst on hydrolysis of dextrin was investigated.

## EXPERIMENTAL

### Materials

Vinyl acetate was distilled under ordinary

pressure. Styrene and divinyl benzene were washed with 5-% sodium hydroxide three times to remove the inhibitor, and with water until no alkali was detectable, and then dried with calcium chloride. All other reagents commercially available were used without further purification.

*Copolymerization*

Copolymerization was carried out in a three-necked flask equipped with a stirrer, a condenser, and a thermometer under the following condition.

    Monomer: vinyl acetate, 0—240 g; styrene, 20 g; divinyl benzene, 20 g.

    Initiator: benzoyl peroxide, 1.0 wt % of the total monomer.

    Medium: water, four times that of the total monomer weight.

    Stabilizer: poly(vinyl alcohol), 0.2%; calcium carbonate, 1.0 %.

    Agitation: 650 rpm.

    Temperature: 65°C.

    Reaction time: 30—90 hr.

At a certain time, the reaction mixture was cooled while being stirred, and then filtered. The copolymer particles obtained were washed with hot water, hydrochloric acid, and then again water. The particles were extracted with methanol in a Soxhlet extractor for 24 hr and then dried under vacuum.

*Sulfonation*

The copolymer particles were packed in a glass column and kept at 80°C. Sulfur trioxide gas was then passed through the column for 5 hr. The sulfonated copolymer was washed with 2-*N* sodium hydroxide and water, and then dried under vacuum.

*Saponification*

The copolymer was saponified with sodium hydroxide in methanol while being refluxed for 5 hr. The product was filtered, washed with hot water, and with hydrochloric acid in order to obtain a free-acid-type catalyst, and then with acetone to remove water, and then dried under vacuum.

*Infrared Absorption Spectrum*

The copolymer particles were pulverized and their infrarred absorption spectra were obtained using a double-beam grating spectrometer (Hitachi Seisakusho, Tokyo, Hitachi EPG-3) by the

KBr disk technique.[5] Absorptions at 3420, 1745, 1610, 1500, 1460, 1175 cm$^{-1}$ and other wave lengths in the spectrum were analyzed by the base-line method.

*Determination of the Vinyl Acetate Unit in the Original Copolymer*

The amount of the acetyl group in the original copolymer was determined by the sulfuric acid hydrolysis—steam distillation method.[6] This amount was also determined with an absorbance at 1745 cm$^{-1}$ (ester carbonyl) in the infrared absorption spectrum. The values obtained by the former method were slightly lower than those obtained by the latter, though the accuracy of the values by the former method were higher than those determined by the latter.

*Determination of Functional Groups in the Catalyst*

A given weight of the catalyst was immersed in a given volume of 0.1-*N* sodium hydroxide for 24 hr, and the amount of available sulfonic acid group in the catalyst was estimated from the titration of an aliquot of the supernatant liquid with 0.1-*N* hydrochloric acid.

A given weight of the catalyst was reacetylated using the method of Nakajima,[7] and again the amount of the acetyl group of the product was determined by the sulfuric acid hydrolysis—steam distillation method. The amount of hydroxyl group in the catalyst was calculated from the amount of the acetyl group.

*Determination of the Hydrolysis Rate of Dextrin*

A given weight of this catalyst was added to 50 ml of 0.045 *M* (as anhydroglucose unit) dextrin solution, and maintained at 75°C in a thermostat being shaken with a width of 20 mm and a speed of 72 strokes/min. Aliquots of the supernatant liquid were taken out at intervals to make determination of the amount of reducing sugar by the Somogyi method.[8] The reaction rates were estimated from the slope of the straight lines obtained from the plots of the amount of reducing sugar against the reaction time; the apparent second-order rate constant, $k_2$, was calculated from the reaction rate.

The reaction scheme is as follows.
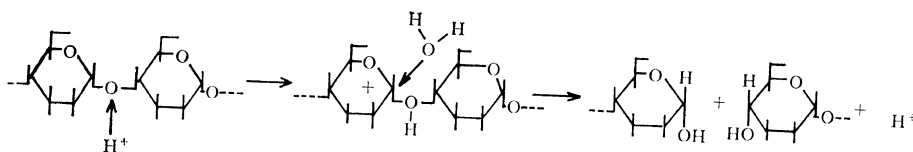
## RESULTS AND DISCUSSION

The ternary suspension copolymerization of vinyl acetate, styrene, and divinylbenzene was examined. The crosslinked copolymer particles were extracted with hot methanol to remove any soluble polymer, and the yield of the insoluble copolymer and vinyl acetate unit wt % in the copolymer were determined. In Figure 1, the yield of insoluble copolymer and vinyl acetate unit wt % in the copolymer are plotted against the reaction time for a reaction mixture of vinyl acetate : styrene : divinylbenzene of 60 : 20 : 20. This yield is seen to increase with reaction time and to level off after 70 hr. The vinyl acetate unit wt % in the copolymer is found to be low initially, and to increase rapidly after 50 hr, and then to level off at exceeding 70 hr. Since, according to Mayo, et al.,[9] the monomer reactivity ratios of styrene (1) and vinyl acetate (2) in the copolymerization are $r_1=55$ and $r_2=0.01$, respectively. We have in-
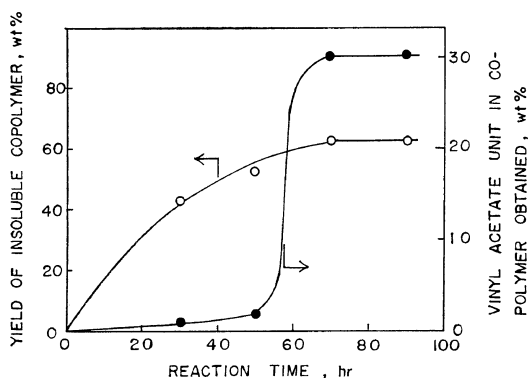


**Figure 2.** Changes in the yield of insoluble copolymer (○) in the vinyl acetate—styrene—divinylbenzene ternary suspension copolymerization at 65°C and in the amount of vinyl acetate unit (●) in the copolymer obtained, as a function of initial wt % of vinyl acetate in the monomer mixture: reaction time, 50 hr.



**Figure 1.** Changes in the yield of insoluble copolymer (○) in vinyl acetate—styrene—divinylbenzene ternary suspension copolymerization at 65°C and in the amount of vinyl acetate unit (●) in the copolymer obtained, as a function of the reaction time: Monomer composition, vinyl acetate: styrene: divinyl benzene=60 : 20 : 20.
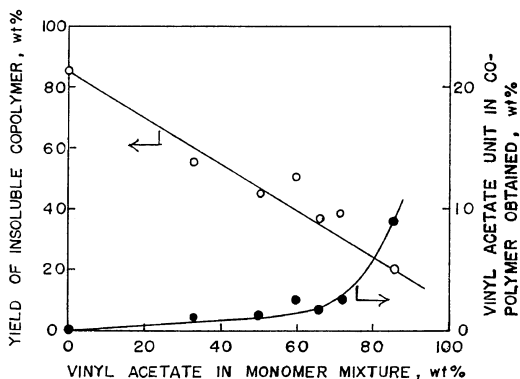
ferred for the present system that at first the styrene is preferentially polymerized into insoluble particles, and that later the vinyl acetate is markedly converted to the polymer. This rapid increase in the vinyl acetate unit in the copolymer after 50 hr is thought to be due to this. The leveling off of the yield and the amount of vinyl acetate unit after the elapse of 70 hr is believed to be due to the considerable decrease in the initiator concentration. The half-life of benzoyl peroxide at 65°C is known to be *ca.* 32 hr.

In Figure 2, the yield of insoluble copolymer and vinyl acetate unit wt % in the copolymer obtained are plotted against the initial wt % of vinyl acetate in the monomer mixture at a reaction time of 50 hr. The yield is seen to decrease with an increasing initial wt % of vinyl acetate in the monomer mixture, and vinyl acetate unit wt % is found to increase with an increasing initial wt % of vinyl acetate monomer slowly in a low concentration range and rather rapidly
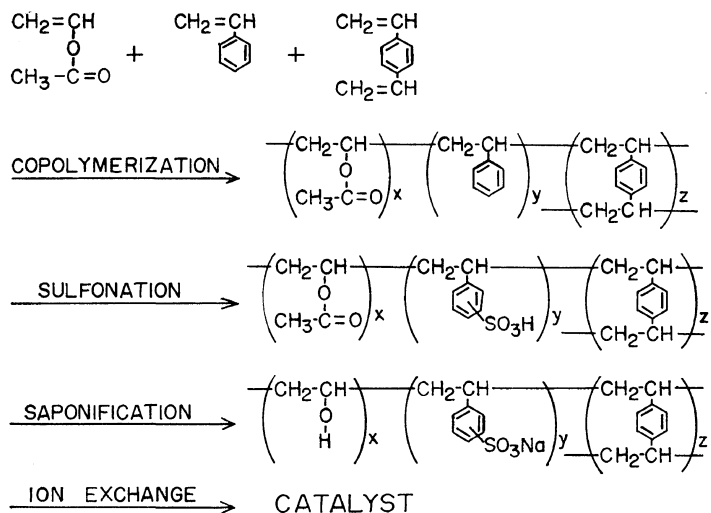
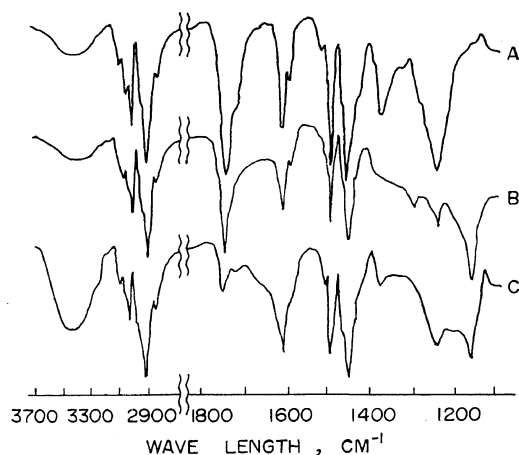**Figure 3.** Reaction scheme examined in the present experiment.



**Figure 4.** Changes in infrared absorption spectrum of a vinyl acetate—styrene—divinylbenzene copolymer with sulfonation and saponification: A, original copolymer; B, sulfonated copolymer; C, saponified copolymer.

at exceeding the 70 wt %. These tendencies may be explained by the monomer reactivity ratios and the reactivity of the monomers to each radical ($k_{11}=178$ and $k_{22}=2040$ $l$/mol sec.[10])

The copolymers, which are white granular particles having a diameter from 0.45—0.55 mm, were sulfonated and saponified. The reaction scheme and changes in the infrared absorption

spectrum observed with the reactions are shown in Figures 3 and 4, respectively. In a spectrum of the original copolymer (A), an absorption at $1745$ $cm^{-1}$ is assigned to the ester carbonyl and absorptions at 1610, 1500, and 1460 $cm^{-1}$ are

**Table I.** Functional groups in the copolymers used for hydrolysis of dextrin as catalysts, with the apparent second-order rate constant, $k_2$, of the hydrolysis

| No. | Vinyl acetate[a] unit | Vinyl alcohol[b] unit | Sulfonic acid[c] group, meq/g | $k_2 \times 10^5$ $l$ mol$^{-1}$min$^{-1}$ |
|---|---|---|---|---|
| 1 | 0 | 0 | 0.21 | 8.6 |
| 2 | 0.6 | 0.2 | 0.89 | 8.1 |
| 3 | 1.0 | 0.7 | 1.51 | 8.3 |
| 4 | 2.8 | 2.6 | 1.15 | 14.9 |
| 5 | 2.5 | 1.6 | 1.17 | 20.4 |
| 6 | 3.4 | 3.1 | 2.66 | 16.4 |
| 7 | 12.7 | 9.5 | 1.19 | 39.8 |
| 8 | 1.1 | 0.7 | 0.48 | 11.8 |
| 9 | 37.5 | 20.1 | 1.16 | 43.6 |
| 10 | 34.8 | 23.2 | 0.22 | 56.2 |
| 11 | 34.8 | 20.8 | 0.98 | 67.3 |

[a] As repeating unit mol % in the original copolymer before saponification.

[b] As repeating unit mol % in the catalyst copolymer after saponification.

[c] In the catalyst copolymer after saponification.

assigned to the benzene ring. For a sulfonated copolymer (B), an additional absorption at 1175 cm$^{-1}$ is found and this is assigned to the sulfonate group. After saponification (C), an increase in an absorption at 3450 cm$^{-1}$ and a decrease in an absorbance at 1745 cm$^{-1}$ are found; the former is assigned to the hydroxyl group. These results indicate that the reactions have proceeded exactly according to the scheme shown in Figure 3.

In Table I, the amounts of the functional groups in the catalyst copolymer prepared with various reaction times and the monomer compositions are listed. It is found that the amount of hydroxyl group in a catalyst copolymer after saponification is smaller than the amount of acetyl group in the corresponding original copolymer before saponification. In general, poly-(vinyl acetate) is known to have a considerable number of side chains formed by chain transfer to the acetyl group of the polymer during poly-merization, and these side chains are readily split from the main chain by saponification.[11] Thus, the difference in the amounts of the acetyl group in the original copolymer and the hydroxyl group in the catalyst copolymer is thought to result from splitting and dissolution of the side chains. Consequently, the amount of vinyl alcohol unit in the catalyst copolymer prepared in the present experiment is limited to ca. 23 mol % because of dissolution of the vinyl alcohol sequence through saponification, as well as by the unfavorable reactivity ratios of the monomers used in the copolymerization system. In the last column of the table, the apparent second-order rate constant, $k_2$, defined as (re-action rate)/[sulfonic acid]·[substrate], of the hydrolysis of dextrin in the presence of the catalyst copolymer are given.

The $k_2$ is plotted against the amount of the hydroxyl group in the copolymer catalyst in Figure 5. The tendency of the hydrolysis rate of dextrin to increase with increasing hydroxyl group concentration in the copolymer is clearly seen in the figure, although this plot is rather scattered out. The $k_2$'s scarcely changed with the addition of copolymer particles which had a vinyl alcohol sequence but not any sulfonic acid group. The maximum reaction rate ob-tained for this experiment is ca. nine fold that of the reaction in the presence of the catalyst without any hydroxyl group. This rate enhance-ment is due perhaps to the substrate binding effect of the hydroxyl group introduced to the catalyst, just as in the homogeneous system,[3] although the Michaelis—Menten kinetics behavior of the reaction rate is not clear. More detailed discussions are being carried out along with investigations of kinetics and selectivity.
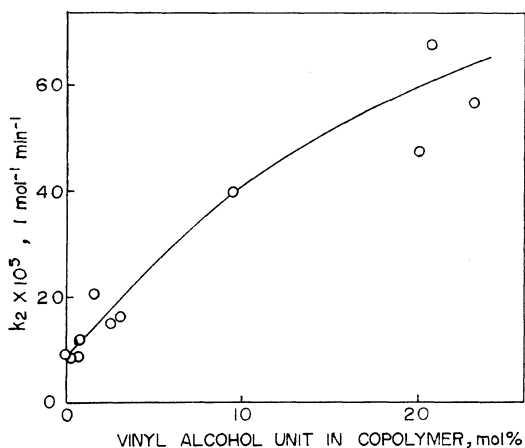


**Figure 5.** Plot of the apparent second-order rate constant, $k_2$, of hydrolysis of dextrin in the presence of the copolymer catalyst at 75°C against the amount of vinyl alcohol unit in the copolymer.

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