

Preparation of Poly(vinyl Alcohol)-Grafted Ion Exchange Resin and Its Catalytic Activity. I. Photo-Induced Graft Copolymerization of Vinyl Acetate on Ion Exchange Resin

KENICHIRO ARAI and YOSHITAKA OGIWARA, *Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan*

Synopsis

Photo-induced graft copolymerization of vinyl acetate on sulfonic acid-type ion exchange resins was investigated. In the copolymerization on isopropylated resin, graft copolymers with graft ratios (mole ratio of monomer unit of grafts to that of the resin) of up to 0.18 were obtained, although in the copolymerization on the original resin graft copolymer was not obtained. It was found that the graft ratio showed a maximum with reaction time, and the maximum graft ratio increased with conversion of the resin from the Na salt to the Fe(III) salt. Poly(vinyl alcohol)-grafted resins were obtained with saponification of the poly(vinyl acetate)-grafted resins, and their catalytic activities on the hydrolysis of amylose were investigated. The catalytic activity of the resins was found to increase with increasing graft ratio at values above 0.10. In the present experiment, however, the maximum acceleration of the reaction was up to 1.5-fold that of the original resin because of limited graft ratio.

INTRODUCTION

The hydrolyses of carbohydrates in the presence of copoly(vinyl alcohol-vinylsulfonic acid) have been studied in a series of investigations.^{1,2} The copolymers were found to have a higher catalytic activity than sulfuric acid, simple sulfonic acid, and poly(vinylsulfonic acid). This rate enhancement was explained in terms of hydrogen-bonding interactions between the substrate and the vinyl alcohol unit in the copolymer, and the electrostatic interactions between the polyanions and protons.

In the present series of papers, the preparation of heterogeneous polymeric catalysts which contain sulfonic acid groups and poly(vinyl alcohol) chains is examined, and their catalytic activities on the hydrolysis of carbohydrates are investigated. Generally, heterogeneous catalysis has lower activity than homogeneous catalysis for the same reaction. However, a heterogeneous catalyst is advantageous because isolation of products and regeneration of the catalyst can be easily accomplished. In order to utilize such advantages, the fixation of enzyme has been a subject of numerous investigations.³

In the present paper, first photo-induced graft copolymerization of vinyl acetate on sulfonic acid-type ion exchange resins is investigated. The copolymers obtained are saponified to poly(vinyl alcohol)-grafted resins, and

then the catalytic activity of the saponified copolymers on the hydrolysis of amylose is studied.

EXPERIMENTAL

Materials

Commercially available sulfonic acid-type ion-exchange resin (Amberlite 120B) and amylose (Sigma Chem. Co., Mo.) were used without further modification. Vinyl acetate was distilled under ordinary pressure and used for copolymerization. All other chemicals used were reagent grade.

Isopropylation of the Resin

Isopropylation of the resin was carried out by means of the Friedel-Crafts reaction. The following procedure was a modified method of that reported by Metz and Mesrobian.⁴ About 150 g of the resin was suspended in 500 g nitrobenzene. To the suspension was added a solution of 32 g anhydrous aluminum chloride and 80 g isopropyl chloride in 250 g nitrobenzene with vigorous stirring over 2 hr. The reactants were heated to 42°C for 5.5 hr with vigorous stirring. After cooling to room temperature, supernatant liquid was removed and the residual mixture was added drop by drop to a large volume of aqueous 5% potassium hydroxide solution with stirring. The mixture was filtered, washed with water, methanol, and then acetone until the odor of nitrobenzene was no more detectable, and then dried under vacuum. The amount of isopropyl groups substituted in the resin, which was calculated from the increase in weight of the resin, was 0.27 mole per mole styrenesulfonic acid repeating units. In the parallel experiment without isopropyl chloride, the resin did not show any change in weight. From the absorbance at 1360 cm^{-1} in the IR spectrum of the product, the increase in weight was confirmed to be due to the introduction of isopropyl groups into the resin.

Graft Copolymerization

Graft copolymerization was carried out in a hard glass vessel shown in Figure 1. The vessel was filled with the reaction mixture and nitrogen atmo-

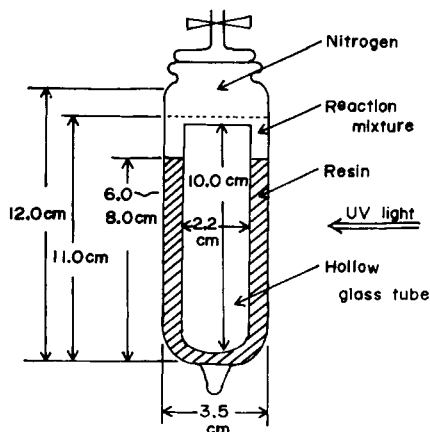


Fig. 1. Reaction vessel for photo-induced graft copolymerization.

sphere, sealed, and then set in a Riko rotary photochemical reactor (Riko Kagaku Co., Tokyo) with a Toshiba high-pressure mercury lamp (H-400P). The vessel was rotated with a speed of 5 rpm while revolving with a speed of 1 rpm around the lamp during the irradiation with UV light. After a given time, the reaction mixture was filtered and extracted with methanol in a Soxhlet extractor for 24 hr, then dried under vacuum. The graft ratio was calculated from the increase in weight of the resin. From the absorbance at 1750 cm^{-1} in the IR spectrum of the product, the increase in weight was confirmed to be due to the grafting of poly(vinyl acetate) onto the resin. The graft ratio was defined as follows;

$$\text{graft ratio} = \frac{\frac{(\text{weight increase})}{(\text{molecular weight of vinyl acetate unit})}}{\frac{(\text{original weight of resin})}{(\text{molecular weight of styrenesulfonic acid unit})}}$$

The filtrate was poured into a large amount of water with stirring, and coagulated poly(vinyl acetate) was recovered, and then dried under vacuum.

Saponification of Poly(vinyl Acetate)-Grafted Resin

About 16 g poly(vinyl acetate)-grafted resin was suspended in 50 ml boiling methanol with refluxing. To the suspension was added dropwise 50 ml 2*N* potassium hydroxide-methanol solution with gentle stirring, and refluxing was continued for 2 hr. After the addition of 50 ml water, the mixture was refluxed for another 5 hr. The reaction mixture was filtered, washed thoroughly with pure water, diluted aqueous hydrochloric acid, and again pure water, and then dried under vacuum. A given weight of poly(vinyl alcohol)-grafted resin was immersed in a given volume of 0.1*N* sodium hydroxide aqueous solution for 24 hr, and the amount of available sulfonic acid in the resin was estimated from the titration of an aliquot of the supernatant liquid with an aqueous solution of 0.1*N* hydrochloric acid.

The reaction scheme examined in the present experiment is shown in Figure 2.

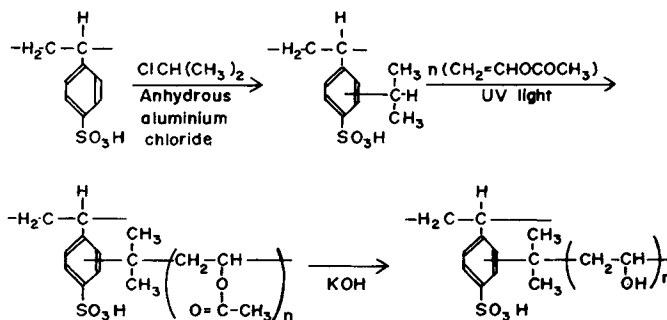


Fig. 2. Reaction scheme examined in the present experiment.

Determination of Hydrolysis Rate of Amylose

Concentrations of substrate and catalyst were 0.045M (as anhydroglucose unit) and 0.900N (as sulfonic acid), respectively. The reaction mixture was 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 and were used for the determination of the amounts of reducing sugar according to the Somogyi method.⁵ The reaction rates were estimated from the slope of the straight lines obtained in the plots between the amounts of reducing sugar and reaction time.

RESULTS AND DISCUSSION

As a preliminary experiment, photo-induced graft copolymerization of vinyl acetate on the original ion exchange resin was examined. However, no change in weight of the resin was observed by the treatment. This result may suggest that the α -hydrogen of the styrenesulfonic acid repeating unit is not labile enough to allow grafting.

Subsequently, isopropylation of the resin was carried out, and graft copolymerization of vinyl acetate on the modified resin was examined. The tertiary hydrogen of the isopropyl group is known to be relatively labile toward UV light.

Figure 3 shows the changes in graft ratio with reaction time. The reaction mixtures consisted of 30 ml vinyl acetate, 30 ml methanol, and 15 g of the isopropylated resin. The reaction temperature was 40°C. In Figure 2, it is found that the graft ratio initially increased with reaction time, showed a maximum at about 10 hr, and then decreased.

It has been reported that the photosensitizer increases the graft ratio in the photo-induced graft copolymerization, and Ogiwara et al.⁶⁻⁸ found that Fe(III) showed a remarkable photosensitizing effect. A comparison between the graft ratio on Fe(III) salt and Na salt of the resin is also made in Figure 3.

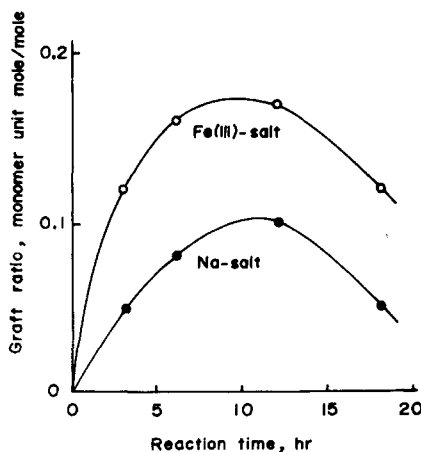


Fig. 3. Graft copolymerization of vinyl acetate on Fe(III) and Na salt of isopropylated ion exchange resin at 40°C. Reaction mixture: vinyl acetate, 30 ml; methanol, 30 ml; resin, 15 g.

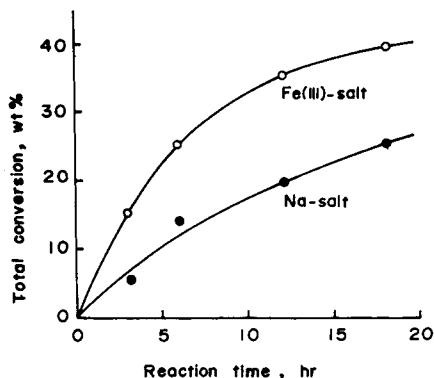


Fig. 4. Total conversion of photo-induced graft copolymerization on Fe(III) and Na salt of ion exchange resin at 40°C. Reaction mixture: vinyl acetate, 30 ml; methanol, 30 ml; resin, 15 g.

The Fe(III) salt is found to give larger graft ratio than the Na salt for the same reaction time, although the shapes of the curves are similar.

Figure 4 shows the total conversion of the polymerization, or total weight per cent of graft and homopolymer to the weight of monomer used, with reaction time. It was found that for both salts of the resin, the total conversions continued to increase with reaction time even after 10 hr, when the maximum graft ratio was found. Therefore, the occurrence of the maximum graft ratio with reaction time shown in Figure 3 was assumed to result from the fact that a part of the grafts initially formed on the resin was removed with further irradiation. In order to confirm the supposition, the change in weight of a grafted resin by irradiation with UV light under the same conditions as grafting was investigated, and the result is shown in Figure 5. It was found that the weight of the grafted resin was decreased slightly but definitely. By irradiation of the ungrafted resin, no change in weight was found. Therefore, the supposition mentioned above may be acceptable.

The effects of some copolymerization conditions on the graft ratio were investigated. Figure 6 shows the graft ratio with reaction time at various reaction temperatures. The graft ratio was found to decrease with rise in tem-

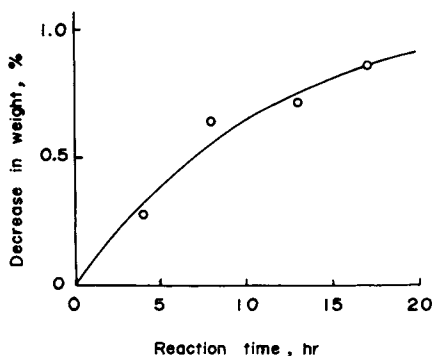


Fig. 5. Decrease in weight of poly(vinyl acetate)-grafted resin with irradiation of UV light. Graft ratio of the resin used, 0.18 mole/mole. Reaction mixture: methanol, 60 ml; resin, 15 g. Temp., 40°C.

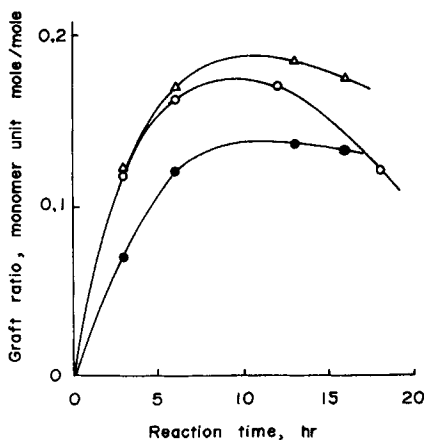


Fig. 6. Graft copolymerization of vinyl acetate on Fe(III) salt of ion exchange resin at various temperatures. Reaction mixture: vinyl acetate, 30 ml; methanol, 30 ml; resin, 15 g. Temp., °C: (Δ) 30; (\circ) 40; (\bullet) 50.

perature. Moreover, the initial rate of graft copolymerization, or the slope of the straight line of the initial graft ratio–reaction time plot, was also found to decrease with rise in reaction temperature, although the total conversion increased. Therefore, the decrease in graft ratio with increasing temperature suggests that the reaction of removal of grafts from the resin was more strongly affected by reaction temperature than the formation of grafts.

Figure 7 shows the influence of the amounts of vinyl acetate in the reaction mixture on the graft ratio. It was found that the graft ratio slightly decreased with increasing the amount of vinyl acetate in the reaction mixture in the range examined in the present experiment. The amount of homopolymer increased remarkably with increasing amount of vinyl acetate.

Furthermore, the influence of a change from hard glass to quartz in the re-

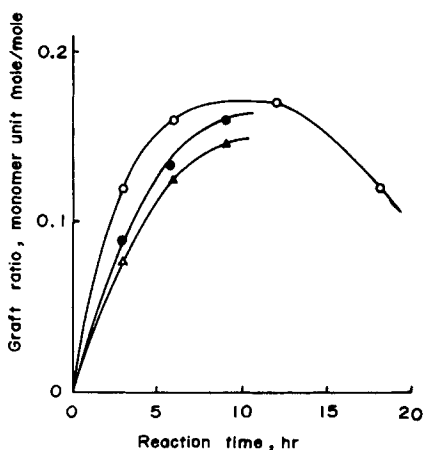


Fig. 7. Graft copolymerization of vinyl acetate on Fe(III) salt of ion exchange resin with various composition of reaction mixture. Resin, 15 g. Temp., 40°C. Reaction mixture: (\circ) vinyl acetate, 30 ml and methanol, 30 ml; (\bullet) vinyl acetate, 45 ml, and methanol, 15 ml; (Δ) vinyl acetate, 60 ml, and methanol, 0 ml.

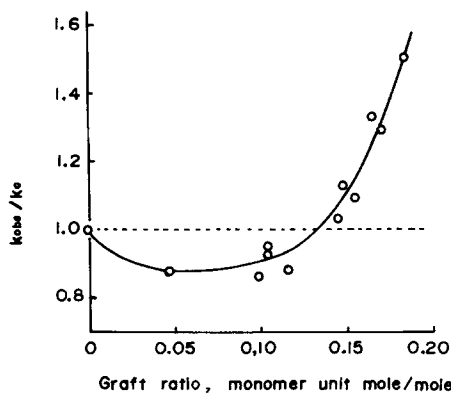


Fig. 8. Catalytic activity of poly(vinyl alcohol)-grafted ion exchange resin on hydrolysis of amylose at 75°C. Substrate concn., 0.045M, catalyst concn., 0.900N.

action vessel was investigated to study the influence of wavelength of irradiating UV light. Little difference was detected except for a remarkable increase in the amount of homopolymer.

Such little change in graft ratio with changing reaction conditions suggests that only a small amount of resin near the surface of the reaction vessel was actually receiving UV light and contributing to the formation of grafts. In other word, the area irradiated may be the predominant factor for graft ratio. This presumption was supported by the fact that the graft ratio decreased with decrease in irradiation area resulting from the removal of a hollow glass tube in the reaction vessel (see Fig. 1).

The poly(vinyl acetate)-grafted resin was washed with diluted aqueous hydrochloric acid to remove Fe(III) and then saponified to poly(vinyl alcohol)-grafted resin. In general, poly(vinyl acetate) has a considerable number of side chains which are formed by the chain transfer to acetyl group of the polymer during polymerization, and the side chains are readily split from the main chain with saponification.^{9,10} Therefore, in the saponification of the poly(vinyl acetate)-grafted resin, a larger decrease in weight than theoretically calculated without taking into consideration side chains was conjectured. In practice, however, the decrease in weight of the grafted resins was between 45 and 55 wt-% of poly(vinyl acetate) grafts, which approximately agreed with the theoretical value (48.8%).

Figure 8 shows the catalytic activity of poly(vinyl alcohol)-grafted resin on the hydrolysis of amylose. The ordinate is expressed as the ratio of the reaction rate in the presence of the grafted resin to the rate in the presence of the untreated original resin, and the abscissa, as the graft ratio. It was found that above a graft ratio of 0.10, the catalytic activity of the grafted resin increased with increasing graft ratio, although in the range up to 0.13 the catalytic activity of the grafted resin is slightly lower than that of the original resin. However, in the present experiment, the maximum acceleration of the reaction was limited up to 1.5-fold, because of the limited graft ratios experimentally achieved.

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