

Preparation of Copoly(vinyl Alcohol–Styrenesulfonic Acid) Resin and Its Catalytic Activity on Hydrolysis of Carbohydrates. II. Two-Step Polymerization using Tetraethylthiuram Disulfide as an Initiator

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Synopsis

Copoly(vinyl alcohol–styrenesulfonic acid) resin was prepared by a two-step polymerization, consisting of a suspension polymerization of styrene containing divinylbenzene using tetraethylthiuram disulfide as an initiator and a subsequent block copolymerization of vinyl acetate to the crosslinked polystyrene obtained, followed by sulfonation and saponification. Some reaction conditions in the polymerization of styrene were investigated to obtain copolymer containing more vinyl alcohol units. The catalytic activity of the copolymer on the hydrolysis of dextrin was investigated and found to be increased with increasing amount of vinyl alcohol units and with a lowering degree of crosslinking of the copolymer. The maximum acceleration of rate obtained in the presence of the copolymer was about six times that in the presence of Amberlite 120B. Catalytic activity of the copolymer on hydrolysis of sucrose and methyl acetate were also investigated and found to be comparable each other and lower than that for dextrin. The difference between the activities for dextrin and for sucrose and methyl acetate increased with an increasing amount of vinyl alcohol units in the copolymer.

INTRODUCTION

In previous work, preparation of copoly(vinyl alcohol–styrenesulfonic acid) resin was investigated by a photoinduced graft polymerization of vinyl acetate on a styrenesulfonic acid type ion exchanger with subsequent saponification,¹ and by a suspension copolymerization of styrene, divinylbenzene, and vinyl acetate, followed by sulfonation and saponification.² In the investigations on catalytic activities of the resins on hydrolysis of dextrin and amylose, the maximum acceleration of the reactions was up to about seven times that in the presence of the resin without vinyl alcohol units. A tendency for the activities to increase with an increasing amount of vinyl alcohol units in the copolymer was also found.

Preparation of soluble copolymers of vinyl alcohol and styrenesulfonic acid have been investigated, and the block copolymers with vinyl alcohol units up to about 90 mole % were obtained by a two-step polymerization, consisting first of a polymerization of styrene using tetraethylthiuram disulfide (TETD) as an initiator, then a subsequent photoinduced block copolymerization of vinyl acetate to the polystyrene obtained, finally followed by sulfonation and saponification.³

In the present experiment, preparation of the similar copolymer resin was carried out by a two-step polymerization, consisting of a suspension polymer-

ization of styrene containing divinylbenzene using TETD as an initiator, then a subsequent block copolymerization of vinyl acetate to the resin obtained, followed by sulfonation and saponification. Catalytic activities of the copolymer on the hydrolysis of some substrates were also examined.

EXPERIMENTAL

Materials

All reagents were purified as previously reported.^{2,3}

Preparation of the Catalyst Copolymer

First, a suspension polymerization of styrene containing divinylbenzene using TETD as an initiator was carried out in a light protected thermostat, under the following conditions:

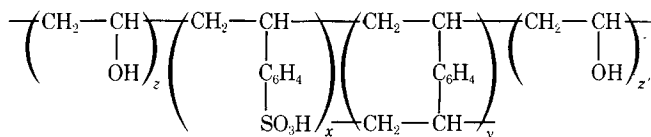
Monomer: styrene 55–40 g, divinylbenzene 5–20 g
 Initiator: TETD 0.6–1.5 g
 Medium: water 300 g
 Stabilizer: poly(vinyl alcohol) 0.05 g, calcium carbonate 3.0 g
 Agitation: 550 rpm (impeller's diameter 6.0 cm)
 Temperature: 80°C, reaction time: 20 hr

After cooling, the reaction mixture was filtered, washed three times with hot water, three times with 1*N* hydrochloric acid, and then with cold water. The obtained crosslinked polystyrene with diethyl dithiocarbamate (DDC) groups at the chain ends, DDC–polystyrene, was extracted with a solvent in a Soxhlet extractor for 24 hr to remove residual unreacted TETD. All these operations were conducted in a light protected chamber to avoid photoinduced degradation of DDC groups in the polymer.

The DDC–polystyrene was used to initiate a polymerization of vinyl acetate with ultraviolet light irradiation under the following conditions:

DDC–polystyrene: 10 g, vinyl acetate: 30 ml
 Solvent: benzene 30 ml, atmosphere: nitrogen
 Temperature: 40°C, reaction time: 40 hr
 Apparatus: Riko rotary photochemical reactor with a reaction vessel made of Pyrex¹

The reaction mixture was filtered, washed, and then extracted in a Soxhlet with methanol to remove vinyl acetate homopolymer. After drying, the block copolymer beads were sulfonated with chlorosulfonic acid and saponified with 1*N* sodium hydroxide methanol and then with 1*N* aqueous solutions. The beads were washed with 1*N* hydrochloric acid to convert the sodium salt to the acid and then washed with water until no soluble acid was detectable. The beads were finally washed with acetone and dried under vacuum at ordinary temperature to avoid the formation of intra- and intermolecular hydrogen bridges in the copolymer. The structure of the catalyst copolymer is as follows:



Functional groups were determined as previously reported.^{1,2}

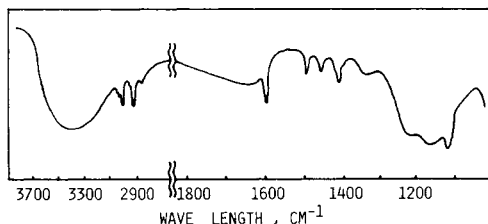


Fig. 1. Typical infrared absorption spectrum of the block copolymer (vinyl alcohol-styrenesulfonic acid).

Determination of Catalytic Activities

Hydrolyses of dextrin, sucrose, and methyl acetate were carried out as previously reported for dextrin,² and the reactions were followed by intermittent determination of reducing sugar,⁴ optical rotatory power,⁵ and acetic acid,⁶ in the reaction mixtures, respectively. Unless otherwise noted, beads of copolymer with a diameter of 0.3–1.0 mm were used for the hydrolysis experiment.

Infrared Absorption Spectrum

Infrared absorption spectra of the copolymers in the catalyst preparation process were obtained as previously reported.² Figure 1 shows a typical infrared absorption spectrum of the catalyst copolymer. The absorptions at 3450 and 1175 cm^{-1} were assigned to hydroxyl and sulfonate groups, respectively.

RESULTS AND DISCUSSION

In order to obtain a block copolymer containing more vinyl acetate units, which would later be converted to vinyl alcohol units in the copolymer catalyst, some reaction parameters in the polymerization of styrene were investigated.

First, the influence of a solvent for extraction of TETD from the DDC-polystyrene on the amount of vinyl acetate unit introduced in the subsequent block copolymerization was examined, because the residual unreacted TETD was believed to interfere with the block copolymerization, with a report by Otsu et al.⁷ and other information. Table I shows the effect of Soxhlet extraction with acetone, benzene, and methanol on the amount of vinyl acetate. It can be seen that the amount of vinyl acetate in the block copolymer is considerably increased

TABLE I
Effect of Soxhlet Extraction of Residual Unreacted Initiator, TETD, from DDC-Polystyrene, with Acetone, Benzene and Methanol, on Amount of Vinyl Acetate Unit Introduced in the Subsequent Block Copolymerization^a

Solvent	Vinyl acetate unit, mole %	
	Copolymer No. 1 ^b	Copolymer No. 2 ^b
Without extraction	3.0	2.8
Methanol	7.0	7.8
Benzene	13.2	14.8
Acetone	14.8	15.4

^a Relative degree of crosslinking, 20%; initiator, TETD, 1.2 g.

^b The copolymers Nos. 1 and 2 differ only in particle size from each other, with average diameters of 0.92 and 0.67 mm, respectively.

by the extraction of residual TETD and that acetone is the preferable solvent for the extraction. In a comparison of copolymers Nos. 1 and 2, varying only in bead size, size of DDC-polystyrene bead is found to only slightly influence the amount of vinyl acetate introduced.

Figure 2 shows the influence of the amount of TETD used in the polymerization of styrene on the amount of vinyl acetate units introduced in the subsequent block copolymerization. The amount of vinyl acetate is found to show a maximum at a definite amount of TETD, although in the lower range of TETD concentration the amount of vinyl acetate increases with an increasing amount of TETD. Again the size of DDC-polystyrene bead is found to have a slight influence on the amount of vinyl acetate.

Figure 3 shows the relationship between the relative degree of crosslinking of polystyrene, expressed as weight percent of divinylbenzene in total monomer in the polymerization of styrene, and the amount of vinyl acetate unit introduced in the subsequent copolymerization. It can be seen that the lower degree of crosslinking gives the more units of vinyl acetate. This tendency is compatible with the fact that in homogeneous block copolymerization systems much higher

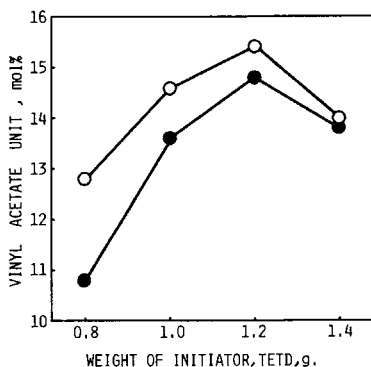


Fig. 2. Influence of the amount of initiator, TETD, in the polymerization of styrene on the amount of vinyl acetate unit introduced to the polystyrene in the subsequent block copolymerization. Relative degree of crosslinking, 17%. (●) Copolymer No. 1 bead with an average diameter of 0.92 mm; (○) copolymer No. 2 bead with an average diameter of 0.67 mm.

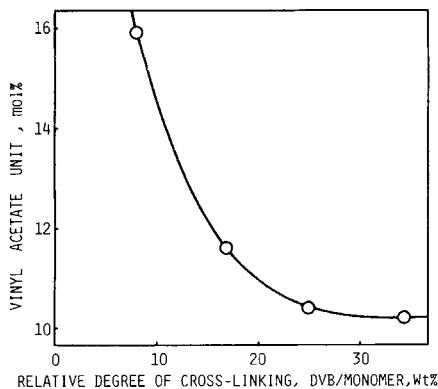


Fig. 3. Relationship between the relative degree of crosslinking of DDC-polystyrene and the amount of vinyl acetate units introduced to the polystyrene in the subsequent copolymerization. Amount of initiator in the polymerization of styrene, TETD, 1.2 g.

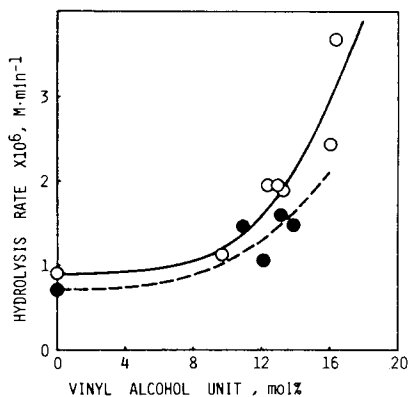


Fig. 4. Dependence of dextrin hydrolysis rate on the amount of vinyl alcohol units in the catalyst copolymer at 80°C. Catalyst concentration 0.10*N*; substrate concentration 0.048*M*. (●) Relative degree of crosslinking 17%; (○) relative degree of crosslinking 8%.

amounts of vinyl acetate can be added to the polystyrene.³ However, the block copolymer beads with a relative degree of crosslinking less than 8% were brittle and not preferable for use as a heterogeneous catalyst.

On consideration of these results, block copolymers containing vinyl acetate unit of up to 24 mole % were prepared. The copolymer beads were sulfonated, saponified, and then washed with 1*N* hydrochloric acid to obtain the catalyst copolymers. Since a part of vinyl acetate sequences was split in the saponification process, as is well known,⁸ the amount of vinyl alcohol units in the catalyst copolymer was redetermined by reacetylation of the copolymer, followed by estimation of the acetyl group with the sulfuric acid hydrolysis–steam distillation method. The maximum amount of vinyl alcohol unit in the catalyst copolymer was about 16 mole %, which was derived from the block copolymer containing vinyl acetate unit of about 24 mole %.

The catalytic activity of the copolymers on the hydrolysis of dextrin was investigated. Figure 4 shows the relationship between the hydrolysis rate of

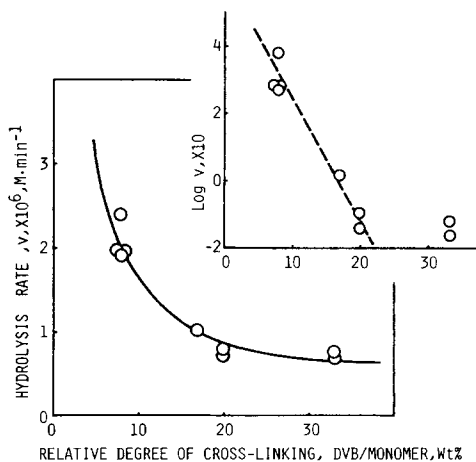


Fig. 5. Change in the hydrolysis rate of dextrin with the relative degree of crosslinking at 80°C. Catalyst concentration 0.10*N*. Substrate concentration 0.048*M*. The amount of vinyl alcohol units in the copolymers is in a range of 11.5–15.0 mole %.

TABLE II
 Comparison of Second-Order Rate Constants k_2 's for Hydrolyses of Dextrin, Sucrose, or Methyl Acetate in the Presence of the Copolymer Catalysts at 70°C

Catalyst	Functional group		Substrate					
	-OH mole %	-SO ₃ H equiv g ⁻¹	Dextrin		Sucrose		Methyl acetate	
			$k_2 \times 10^5$ M ⁻¹ min ⁻¹	k_2/k_A^a	k_2 M ⁻¹ min ⁻¹	k_2/k_A^a	k_2 M ⁻¹ min ⁻¹	k_2/k_A^a
Catalyst No. 6	16.3	5.43	10.5	5.97	0.128	1.27	0.177	1.23
Catalyst No. 7	9.6	5.07	3.60	2.05	0.080	0.79	0.150	1.05
Catalyst No. 0	0	4.78	2.30	1.30	0.122	1.19	0.166	1.16
Amberlite 120B	0	1.57	1.76	1.00	0.101	1.00	0.143	1.00

^a k_2/k_A : the ratio of each k_2 against that in the presence of Amberlite 120B for the same substrate. Relative degree of crosslinking of the copolymer; 8%.

dextrin and the amount of vinyl alcohol units in the catalyst copolymer. The rates are found to increase with an increasing amount of vinyl alcohol unit for both series with different degrees of crosslinking, 8 and 17%.

Figure 5 shows the relationship between the rate of hydrolysis and the relative degree of crosslinking of the catalyst copolymer. The reaction rate increases with lowering degree of crosslinking, although it is scattered mainly because of the difference in the amount of vinyl alcohol units in the copolymer; vinyl alcohol unit in the copolymers used for the plot is in a range of 11.0–15 mole %. The faster rate of reaction with the lower degree of crosslinking is compatible with the fact the soluble copoly(vinyl alcohol–styrenesulfonic acid) showed far higher catalytic activity in the hydrolysis of dextrin.³ Bodamer and Kunin⁹ reported a linear relationship between the logarithm of the reaction rate and the degree of crosslinking in the hydrolysis of sucrose in the presence of sulfonic acid type ion exchangers. The same relationship is also found in the present reaction system, as shown in Figure 5, except for the higher degree of crosslinking. The deviation may be explained by an assumption that the substrate, especially a high-molecular-weight molecule such as dextrin, can scarcely penetrate into the interior of the catalyst bead with the higher degree of crosslinking, so further increase in the degree of crosslinking hardly influences on the reaction rate.

Catalytic activities of the copolymer on hydrolysis of some other substrates were also investigated and compared. Table II shows the second-order rate constants k_2 's, of hydrolysis of dextrin, sucrose, and methyl acetate in the presence of the copolymers or Amberlite 120B (acid form). For sucrose and methyl acetate the relative catalytic activities k_2/k_A , based on that of Amberlite 120B, of each copolymer are found to be comparable to each other for all copolymers, although the activities themselves are slightly changed with an increasing amount of vinyl alcohol units in the copolymers. For dextrin, however, the relative catalytic activity of the copolymer also increases with an increasing amount of vinyl alcohol units, and the difference between the activities for dextrin and for sucrose and methyl acetate increases with an increasing amount of vinyl alcohol units.

These results suggest that the poly(vinyl alcohol) sequences in the copolymer interact with the hydroxyl groups of the polymeric substrate, probably because of hydrogen bonding,⁵ so that the hydrolysis of dextrin is accelerated. The copolymer does not interact with low molecular weight substrates, even when one contains hydroxyl groups. Therefore, the catalytic activities of the copolymer for hydrolysis of sucrose and methyl acetate is not affected very much by the content of vinyl alcohol unit in the copolymer.

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