

Grafted Chain as Spacer for an Insoluble Polymer Catalyst

INTRODUCTION

Insoluble polymer catalysts are more favorable from the viewpoint of recovery of the catalysts and of the products, although the catalytic activity of the insoluble catalyst is usually lower than that of the soluble one. We have studied the improvement of the catalytic activity of the insoluble catalyst by the introduction of grafted chain as spacer between the insoluble matrix and the functional group.¹⁻⁴ In a previous paper,⁴ in order to increase the percent grafting in the graft copolymerization, two-step polymerization consisting of a suspension polymerization of styrene containing a small amount of divinylbenzene using tetraethylthiuram disulfide as an initiator and then a subsequent polymerization of chloromethylstyrene onto the crosslinked polystyrene bead was carried out. Considerable increases in both percent grafting and grafting efficiency were found. Furthermore, the iminodiacetic acid group as ligand group was introduced on the grafted chain and the catalytic activity of the complex with Cu(II) on the decomposition of hydrogen peroxide was examined. The catalytic activity was improved with the introducing grafted chain as spacer, especially markedly at higher percent grafting.

In the present experiment, a polystyrene-grafted crosslinked polystyrene bead was prepared with the same method and then sulfonated. The catalytic activity of the obtained sulfonated polystyrene bead on the hydrolysis of sucrose was examined to investigate the effect of grafted chain as spacer on the catalytic activity.

EXPERIMENTAL

Reagents

Styrene was purified by vacuum distillation in a stream of nitrogen. Divinylbenzene was washed with 5% sodium hydroxide three times to remove the inhibitor, with water until no alkali was detectable, and then dried with calcium chloride. All other reagent-grade chemicals commercially available were used without further purification.

Preparation of Crosslinked Polystyrene Bead

A crosslinked polystyrene bead was prepared with the method previously reported.⁴

Graft Polymerization of Styrene onto the Bead

Graft polymerization was carried out with an apparatus previously reported.^{1,2} Two grams of the crosslinked polystyrene bead containing diethyldithiocarbamate group at the chain end (DDC-polystyrene) in 15 mL of mixture of styrene and benzene (1:1 in volume) was irradiated with UV light at 60°C. After a given time, the reaction mixture was filtered and the insoluble polymer was extracted with benzene in a Soxhlet extractor for 24 h, and then dried under vacuum. The filtrate, together with the extracting benzene, was added to a large excess volume of methanol to precipitate the homopolystyrene.

Sulfonation of the Grafted Polystyrene Bead

Sulfonation of the grafted polystyrene beads was carried out with two methods. A part of the beads was sulfonated with an usual sulfonation method using concentrated sulfuric acid.⁵ Another part of the beads was sulfonated with the method reported by Signer et al.⁶: 2.6 g of the bead was added to 28 mL of 1,4-dioxane (2.6 g)-sulfur trioxide (2.0 g) adduct-suspending 1,2-dichloroethane and kept at room temperature. After a given time, the reaction mixture was added to a large excess volume of water, filtered, washed with 1N sodium hydroxide, washed with water until no

alkali was detectable, and then dried under vacuum. A part of the sulfonated beads was washed with 0.1N hydrochloric acid to convert it to free acid form and analyzed for the amount of sulfonic acid group in the bead: A given amount of the sulfonated beads was immersed in a 50 mL of 0.1N sodium hydroxide for 24 h, and an aliquot of the supernatant liquid was extracted and titrated with 0.1N hydrochloric acid to estimate the amount of sulfonic acid group in the bead.

Catalytic Activity of the Sulfonated Bead on Hydrolysis of Sucrose

One gram of free acid-form sulfonated beads was added to 100 mL of 0.1 mol L⁻¹ aqueous solution of sucrose and maintained at 75°C in a thermostat being shaken with a width of 20 mm and a speed of 72 strokes min⁻¹. Aliquots of the supernatant liquid were taken out at intervals for the determination of the optical rotatory power with a polarimeter. The pseudo-first-order rate constant k_1 was calculated from the straight line obtained in the pseudo-first-order plot of these data, and the second-order rate constant k_2 was calculated from the k_1 .

RESULTS AND DISCUSSION

In the graft polymerization of styrene onto DDC-polystyrene bead under UV light irradiation, graft polymers with percent grafting of 69, 175, and 215% were obtained with grafting efficiency of more than 80%. The grafted beads, together with the original beads, were sulfonated with two methods. On the left-hand side of Figure 1, the amount of sulfonic acid group introduced into the grafted beads with the usual sulfonation method using concentrated sulfuric acid are plotted against the reaction time. This sulfonation method is known to be facile but does yield crosslinking between polystyrene chains.⁶ In the figure, the amount of sulfonic acid group are found to increase up to about 4.0 mmol g⁻¹ with the reaction time and decrease slightly with increasing percent grafting at the same reaction time. On the right-hand side of Figure 1, the similar plots with a sulfonation method using 1,4-dioxane-sulfur trioxide adduct are shown. The sulfonation method is claimed to yield no crosslinking between the polystyrene chains.⁶ Also in this case, the amounts of sulfonic acid group introduced are found to increase with the reaction time, but they show a tendency to level off at a higher amount range and are limited up to about 2.8 mmol g⁻¹, the value being rather less than those obtained with concentrated sulfuric acid.

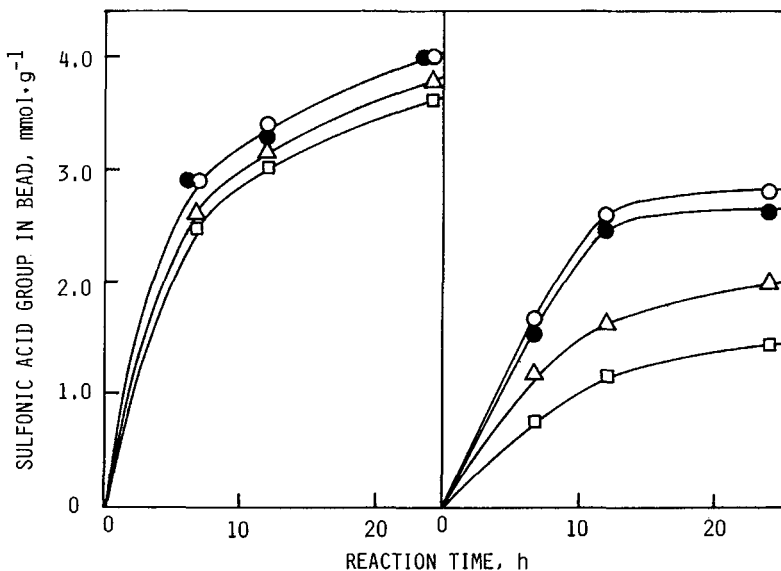


Fig. 1. Plots of the amount of sulfonic acid group introduced into the grafted bead by sulfonation with concentrated sulfuric acid (left-hand side) and with 1,4-dioxane-sulfur trioxide adduct (right-hand side) against the reaction time. Percent grafting of the bead used (%): (○) 0; (●) 69; (△) 175; (□) 215.

TABLE I
Second-Order Rate Constant k_2 , for Hydrolysis of Sucrose in the Presence of Sulfonated Polystyrene-Grafted Crosslinked Polystyrene Beads at 75°C

Sulfonation	Percent grafting (%)	Sulfonic acid group in bead (mmol g ⁻¹)	k_2 (10 ⁻² L mol ⁻¹ min ⁻¹)
With 1,4-dioxane-sulfur trioxide adduct	0	1.58	1.69
		2.59	1.51
		2.80	1.50
	69	1.53	1.80
		2.50	1.71
		2.65	1.71
		1.20	2.07
		1.64	2.03
	175	2.00	2.00
		0.50	2.20
		1.16	2.17
		1.45	2.15
With concd sulfuric acid	0	2.87	1.26
		3.40	1.15
		4.00	1.01
	69	2.90	1.06
		3.30	0.96
		4.02	0.89
		2.66	0.94
		3.20	0.80
	175	3.81	0.68
		2.51	0.89
		3.05	0.75
		3.64	0.58

Furthermore, the amounts of sulfonic acid group are found to decrease considerably with increasing percent grafting at the same reaction time. These results may be due to that the sulfonation with 1,4-dioxane-sulfur trioxide adduct is restricted to the styrene units on the surface of the bead because of solid-solid reaction, in contrast to the sulfonation with concentrated sulfuric acid in which sulfuric acid penetrates also into the inside of the bead to sulfonate the styrene units. Decrease in the amount of sulfonic acid group with increasing percent grafting may be explained by the fact that the diameter of the bead considerably increases with increasing percent grafting; the surface area per unit weight available for sulfonation decreases, especially in the reaction with 1,4-dioxane-sulfur trioxide adduct.

Catalytic activity of the sulfonated beads on the hydrolysis of sucrose was examined. Three lots of the beads with different amount of sulfonic acid group were used at the same percent grafting for each sulfonation system. The data are summarized in Table I. Figure 2 shows the plots of the k_2 for the reaction in the presence of the beads sulfonated with concentrated sulfuric acid and 1,4-dioxane-sulfur trioxide adduct against the percent grafting of the beads. In the reaction in the presence of the bead sulfonated with 1,4-dioxane-sulfur trioxide adduct, k_2 is clearly found to increase with percent grafting, while in the reaction in the presence of the bead sulfonated with concentrated sulfuric acid, k_2 decreases, although there is some scattering of the plots with different amount of sulfonic acid group. The increase in k_2 with increasing percent grafting in the former reaction system is believed to result from the fact that the sulfonic acid groups are mostly on the surface of the bead and have more freedom to attack the substrate. Furthermore, the freedom increases with increasing percent grafting because the styrene units to be sulfonated are more separated from the surface of the beads with a higher percent grafting. On the other hand, the sulfonic acid groups introduced with concentrated sulfuric acid are partly inside of the bead, and even the groups on the surface at the initial stage of the reaction can be embedded into the

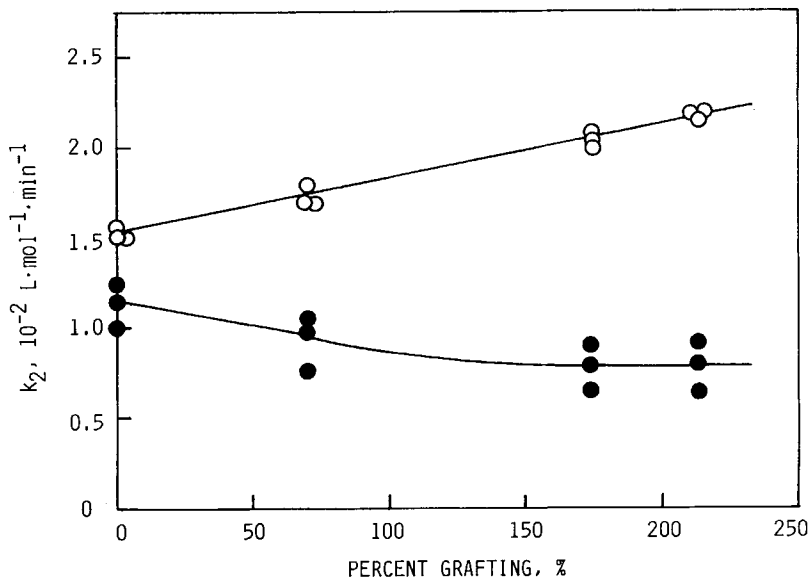


Fig. 2. Plots of second-order rate constant k_2 for the hydrolysis of sucrose in the presence of beads sulfonated with 1,4-dioxane-sulfur trioxide adduct (○) and with concentrated sulfuric acid (●) against the percent grafting of the bead. Three lots of beads with different amount of sulfonic acid group at the same percent grafting were used for each sulfonation system.

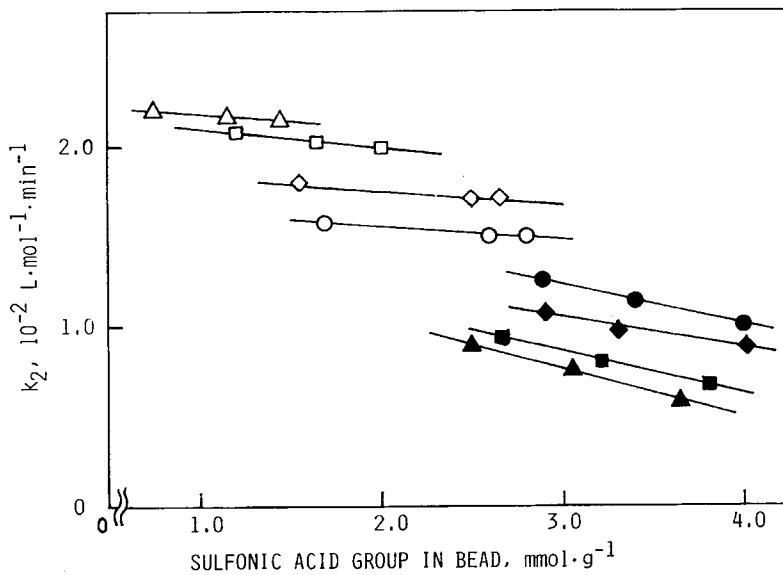


Fig. 3. Plots of k_2 against the amount of sulfonic acid group introduced into the beads sulfonated with 1,4-dioxane-sulfur trioxide adduct (○, ◇, □, △) and with concentrated sulfuric acid (●, ◆, ■, ▲). Percent grafting of the bead used (%): (○, ●) 0; (◇, ◆) 69; (□, ■) 175; (△, ▲) 215.

bead because of the occurrence of crosslinking at the later stage of the reaction, consequently the freedom of the groups to attack the substrate decreasing with increasing percent grafting.

Since a tendency that the bead with less amount of sulfonic acid group gives a higher value of k_2 , the influence of the amount of sulfonic acid group in the bead on the k_2 was examined. Figure 3 shows the plots of the k_2 against the amount of sulfonic acid group in the bead. It is clearly shown that the sulfonation with 1,4-dioxane-sulfur trioxide gives beads containing sulfonic acid group with higher catalytic activity, although the amount of sulfonic acid group introduced is less, comparing with sulfonation with concentrated sulfuric acid. Furthermore, decrease in the catalytic activity with increasing amount of sulfonic acid group introduced is less than the case of the bead sulfonated with concentrated sulfuric acid and the difference between the catalytic activities of beads sulfonated with 1,4-dioxane-sulfur trioxide adduct and concentrated sulfuric acid becomes larger with increasing percent grafting. Therefore, the higher catalytic activity of the bead sulfonated with 1,4-dioxane-sulfur trioxide is believed to be not due to the lesser amount of sulfonic acid group, at least for the beads containing grafted chains.

From these results, it is concluded that the sulfonation with 1,4-dioxane-sulfur trioxide adduct to prepare the insoluble sulfonic acid-type catalyst is preferable to that with concentrated sulfuric acid, especially for the bead with grafted chains, because of limiting the introduced sulfonic acid groups mostly on the surface of the bead and having no crosslinking. The grafted chains introduced on the insoluble matrix contribute to increasing catalytic activity of the sulfonic acid group in the case of sulfonation using 1,4-dioxane-sulfur trioxide adduct, as a spacer.

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