Grafted Chain as Spacer for an Insoluble Polymer Ligand. II. Two-Step Polymerization Using Tetraethylthiuram Disulfide as an Initiator

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Synopsis

In order to increase the percent grafting in the graft polymerization of chloromethylstyrene onto a crosslinked polystyrene bead with UV light irradiation, a two-step polymerization consisting of a suspension polymerization of styrene containing divinylbenzene using tetraethylthiuram disulfide as an initiator and then a subsequent graft polymerization of chloromethylstyrene onto the crosslinked polystyrene bead was carried out. The percent grafting of up to 180% was obtained, the value being about twofold larger than that for the usual method using benzoyl peroxide as an initiator. The higher percent grafting was found to result from the higher grafting efficiency due to the preferential decomposition of diethyldithiocarbamate group in the crosslinked polystyrene bead with UV light irradiation. The chloromethyl group in the grafted chain was converted to aminomethyl group, and then to the iminodiacetic acid group, which was a ligand group. The adsorption behavior of Cu(II) by the ligand polymer and the catalytic activity of the complex in the decomposition of hydrogen peroxide were examined, and both properties were found to be improved by introducing grafted chain as spacer, especially markedly at a higher percent grafting.

INTRODUCTION

In order to improve the functions of an insoluble functional polymer, introducing a spacer between its insoluble matrix and the functional groups has been investigated.[1-5] We have studied the effect of a graft-polymerized graft as a spacer for an insoluble polymer ligand, although the spacer in this case has a different structure from an ordinary spacer in such a way that the ligand groups are separated from the crosslinked polymer bead at a variety of distances. We found that the adsorption behavior of Cu(II) by the polymer ligand and the catalytic activity of the complex in the decomposition of hydrogen peroxide were improved with the introducing spacer. However, in the graft polymerization with UV light irradiation, percent grafting was up to 85% even at high conversion, because of yielding much homopolymer. And the catalytic activity of the complex of the spacer-introduced polymer ligand with Cu(II) was limited up to 2.5-fold larger than that of polymer ligand without spacer, probably because of the lower percent grafting.

In the present experiment, in order to increase the percent grafting, the graft copolymer was prepared by a two-step polymerization, consisting of a suspension polymerization of styrene containing a small amount of divinylbenzene using tetraethylthiuram disulfide (TETD) as an initiator; then a

subsequent graft polymerization of chloromethylstyrene onto the crosslinked polystyrene bead. The chloromethyl group in the grafted chain was converted to amino group, and then to iminodiacetic acid group as a ligand group, and the effect of the grafted chain with a higher percent grafting as a spacer on the adsorption behavior of Cu(II) by the polymer ligand and the catalytic activity of the complex in the decomposition of hydrogen peroxide were examined.

EXPERIMENTAL

Reagents

Styrene and chloromethylstyrene were 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 it was dried with calcium chloride. All other reagent grade chemicals commercially available were used without further purification.

Preparation of Crosslinked Polystyrene Bead

A mixture of 40 mL of styrene and 10 mL of divinylbenzene containing 1.0 g of TETD as an initiator was added to 300 mL of water containing 0.5 g of poly(vinyl alcohol) and 3.0 g of calcium carbonate, and stirred at 90°C in a light-protected thermostat. After cooling, the reaction mixture was filtered, washed three times with hot water, three times with N-hydrochloric acid, and then with cold water. The obtained crosslinked polystyrene with diethyldithiocarbamate (DDC) groups at the chain ends, DDC–polystyrene, were extracted with benzene in a Soxhlet extractor for 24 h to remove residual unreacted TETD. The beads obtained were fractionated to the size of 20–80 mesh and used for the graft polymerization as an insoluble polymer matrix. All these operations were conducted in a light-protected chamber to avoid photoinduced degradation of the DDC group.
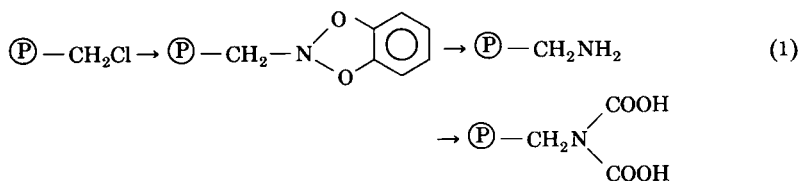
Graft Polymerization

Graft polymerization was carried out with an apparatus previously reported.[4,5] A DDC-polystyrene bead (2.0 g) in 15 mL of chloromethylstyrene benzene solution was irradiated with UV light at 60°C. After a given time, the reaction mixture was filtered and extracted with benzene in a Soxhlet extractor for 24 h, and then dried under vacuum. The filtrate, together with the extracting benzene, added to a large excess volume of methanol to precipitate the homopolystyrene. The percent grafting was defined as [(weight increase in the graft polymer)/(weight of the matrix polymer)] × 100%, and the grafting efficiency as [(weight increase in the graft polymer)/(weight increase in the graft polymer + weight of homopolymer)] × 100%.

Graft polymerization was carried out also for the crosslinked polystyrene bead prepared by the usual method using benzoyl peroxide as an initiator, BPO–polystyrene.

Introducing Ligand Group to the Grafted Chain

Conversion of chloromethyl group of the grafted chain to the aminomethyl group was carried out according to the method reported by Sparrow.[6] First, 20 g of the grafted polymer bead was immersed in 150 mL of dry distilled dimethylformamide (DMF), and equal mole of potassium phthalimide to the chloromethyl group was added. The mixture was stirred at 50°C for 18 h, after which the bead was washed three times each with DMF, methanol, water, and then methanol. After drying, the bead was treated overnight with 1.5 mL of hydrazine hydrate in refluxing ethanol. The reaction mixture was filtered from the hot ethanol and washed three times with ethanol, 5% aqueous potassium hydroxide, water, and then ethanol.

Conversion of aminomethyl group in the grafted chain to iminodiacetic acid group was carried out according to the method reported by Okawara et al.[7] Chloroacetic acid (15 g) was neutralized with a 10% aqueous solution of sodium hydroxide using phenolphthalein. The polystyrene bead (8 g) containing amino group and 30 mL of ethanol were added to the solution, which was stirred at 80°C for 6 h, keeping the reaction mixture basic by means of intermittent addition of dilute sodium hydroxide. The reaction mixture was filtered, washed with dilute hydrochloric acid, with water, and then dried under vacuum. The reaction sequence is as follows:

$$ \text{Ⓟ}-CH_2Cl \rightarrow \text{Ⓟ}-CH_2-N \overset{O}{\underset{O}{\diagup \diagdown}} \rightarrow \text{Ⓟ}-CH_2NH_2 \qquad (1) $$

$$ \rightarrow \text{Ⓟ}-CH_2N \overset{COOH}{\underset{COOH}{\diagup \diagdown}} $$

where Ⓟ is a crosslinked polystyrene bead. The functional group introduced at each reaction step was confirmed with IR adsorption spectrum.

A part of the DDC–polystyrene bead was directly chloromethylated according to the method previously reported,[5] then suffered the same reactions, and was used as a polymer ligand without spacer.

Adsorption of Cu(II) by the Ligand Polymer Bead

Adsorption of Cu(II) by the ligand polymer bead was examined according to the method previously reported.[5]

Catalytic Activity of the Complex of the Ligand Polymer Bead with Cu(II)

Catalytic activity of the complex of the ligand polymer bead with Cu(II) was examined according to the method previously reported.[5]

RESULTS AND DISCUSSION

First, percent grafting in the graft polymerization of chloromethylstyrene onto DDC–polystyrene with UV light irradiation was compared with that onto BPO–polystyrene. Figure 1 shows the plots of the percent grafting
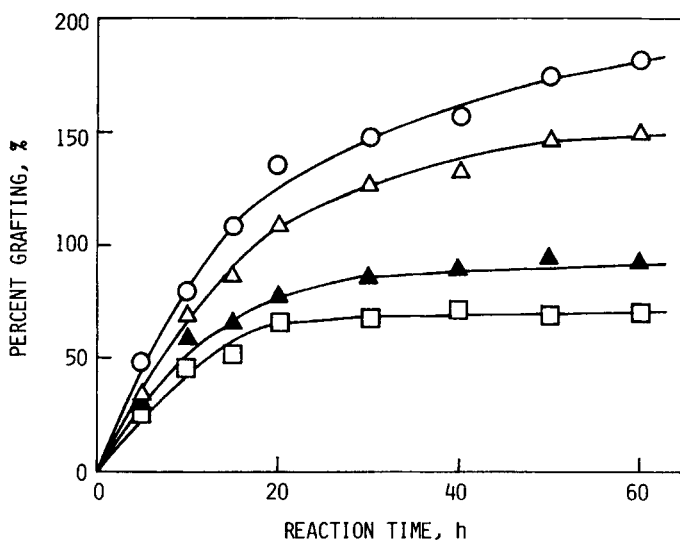
Fig. 1.   Plots of percent grafting against reaction time in the graft polymerization of chloro-methylstyrene onto DDC–polystyrene (○, △, □) and BPO–polystyrene (▲) with UV light irradiation at 60°C. [Chloromethylstyrene] in vol % in benzene: (○) 60; (△, ▲) 50; (□) 35.

against reaction time at some concentrations of chloromethylstyrene in the graft polymerization of chloromethylstyrene onto DDC–polystyrene and BPO–polystyrene. The percent graftings were found to increase with the reaction time and with the concentration of chloromethylstyrene. It is also found that, at the same concentration of chloromethylstyrene, DDC–poly-styrene gives a higher percent grafting than BPO–polystyrene, and, in the case of the former, percent grafting of up to 180% is obtained, the value being about twofold larger than the maximum value obtained for BPO–polystyrene.

In order to clarify the cause of the higher percent grafting, grafting efficiency in the graft polymerizations was examined. Figure 2 shows the plots of the grafting efficiency onto DDC–polystyrene and BPO–polystyrene against the reaction time. It is found that the DDC–polystyrene gives a very high grafting efficiency at the initial stage of the polymerization, indicating that the DDC groups on the DDC–polystyrene are decomposed with UV light irradiation effectively to give initiating sites of the graft polymerization. The grafting efficiency is found to decrease gradually with the reaction time to about 70%, which may result from the decrease in the amount of DDC group; the graft polymerization rate decreases with the decrease in the DDC group, in addition to the decrease in the amount of chloromethylstyrene monomer, while the homopolymerization rate is less affected with reaction time, thereby the grafting efficiency decreases with reaction time. Comparing with the DDC–polystyrene, BPO–polystyrene gives rather lower grafting efficiency at around 50%. Therefore, the higher percent grafting onto DDC–polystyrene than onto BPO–polystyrene is believed to result from the higher grafting efficiency due to photoinduced preferential decomposition of DDC group.

The chloromethyl group in the grafted chain was converted to the aminomethyl group, and then to the iminodiacetic acid group, which is a ligand group. The amount of the iminodiacetic acid group introduced to the
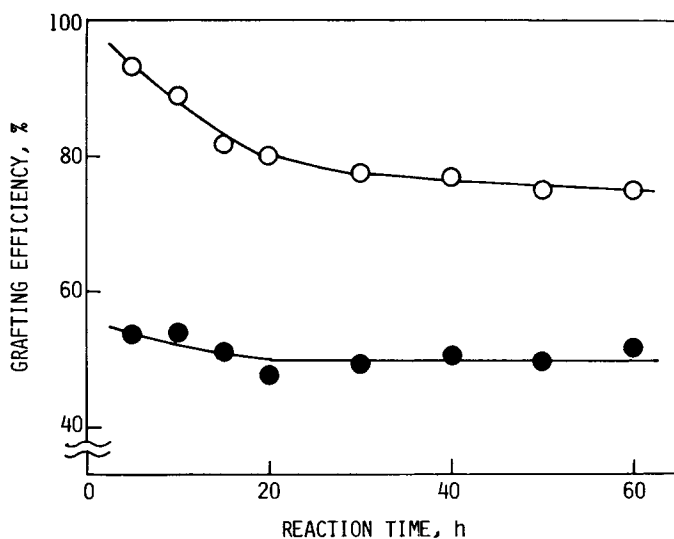
Fig. 2. Plots of the grafting efficiency of chloromethylstyrene onto DDC–polystyrene (○) and BPO–polystyrene (●) against reaction time. [Chloromethylstyrene]: 50 vol % in benzene.

TABLE I

A_s and K in the Langmuir's Adsorption Isotherm for Adsorption of Cu(II)
by the Polymer Ligand, Depending on the Percent Grafting of the Ligand

Percent grafting (%)	IDA content[a]	$A_s{}^{b}$	K (10^4 L mol^{-1})
0	0.78	0.08	0.5
68	0.77	0.25	1.8
123	0.82	0.39	2.9
172	0.92	0.94	3.8

[a] IDA = iminodiacetic acid group in (10^{-3} mol g^{-1} of bead).
[b] A_s is expressed by mol mol^{-1} of IDA group.

grafted polymer obtained from DDC–polystyrene slightly increased with increasing percent grafting, as will be seen in Table I, up to 0.92×10^{-3} mol g^{-1} of bead. The amount of the iminodiacetic acid group introduced to the grafted polymer obtained from BPO–polystyrene was limited to 0.60×10^{-3} mol g^{-1} of bead, probably because of its lower percent grafting.

The adsorption behavior of Cu(II) by the polymer ligand was examined. The upper curves of Figure 3 shows the plots of the amount of adsorbed Cu(II) against the concentration of Cu(II) in the bulk solution. The data were evaluated according to Langmuir's adsorption isotherm:

$$\frac{c}{a} = \frac{1}{K \cdot A_s} + \frac{1}{A_s} \cdot c \tag{2}$$

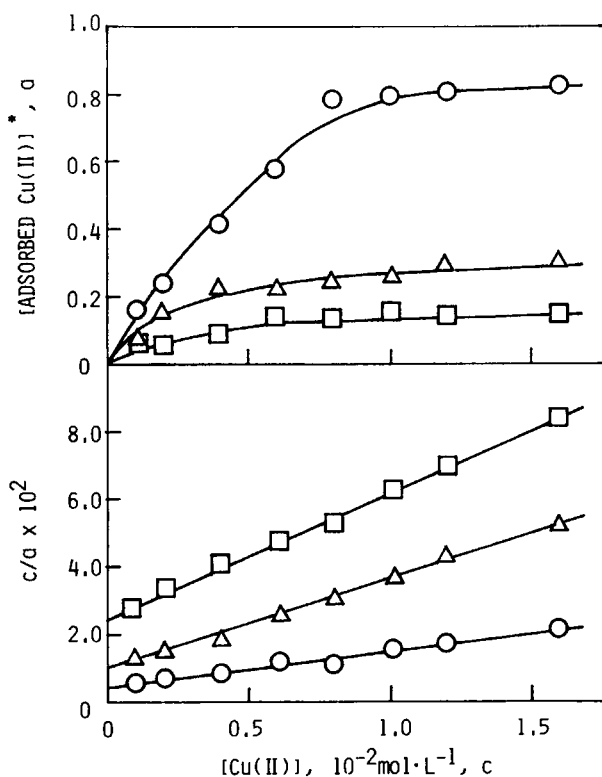where c is the concentration of Cu(II) in the bulk solution, a is the adsorption

Fig. 3. Relationships between the amount of adsorbed Cu(II) by the polymer ligands and concentration of Cu(II) in the bulk solution (upper) and the Langmuir's plots of the data (lower). Percent grafting of polymer ligand: (○) 172%; (△) 123%; (□) 68%. [Ligand polymer]: 1.0×10^{-2} mol of iminodiacetic acid L^{-1}. a is expressed by mol mol^{-1} of iminodiacetic acid. pH: 5.0.

amount of Cu(II), K is the stability constant, and A_s is the saturated adsorption amount of Cu(II). In the lower curves of Figure 3, the plots of c/a against c for the same data are shown. Good straight lines are obtained, which means the adsorption behavior follows Langmuir's adsorption isotherm. The parameters of the equation were calculated from the straight lines and are tabulated in Table I. The value of A_s is found to increase with the increasing percent grafting, especially markedly at higher percent grafting, up to 0.94, the value meaning that 94% of the iminodiacetic acid group introduced in the grafted chain is available for adsorption of Cu(II), being about 3.5-fold larger than the maximum value obtained with BPO–polystyrene. The value of K is also found to increase with the percent grafting. These results may reflect that freedom of the ligand group in the grafted chains to coordinate to Cu(II) increases, especially markedly at higher percent grafting, as the percent grafting increases.

The catalytic activity of the complex of the polymer ligand with Cu(II) on the decomposition of hydrogen peroxide was examined. Figure 4 shows the first-order plots of the decomposition rate of hydrogen peroxide in the copper sulfate aqueous solution (pH 5.0) with addition of the polymer ligand, and
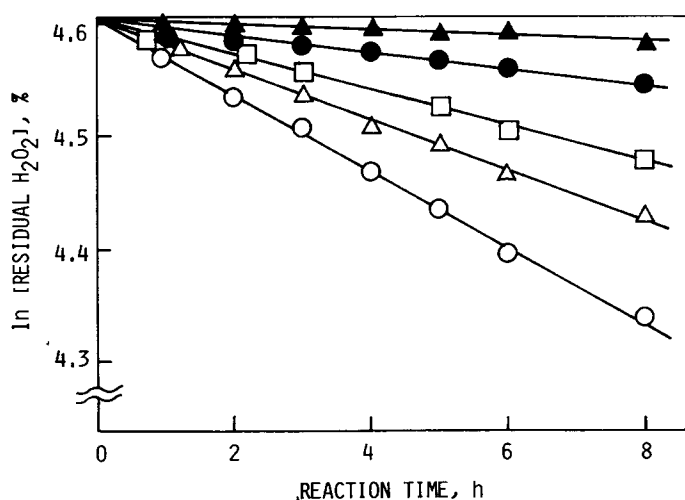
Fig. 4. First-order plots of the residual amount of hydrogen peroxide in copper sulfate aqueous solution in the presence or absence of polymer ligand: (▲) without polymer ligand; (●) polymer ligand with percent grafting 0%; (□) polymer ligand with percent grafting 68%; (△) polymer ligand with percent grafting 123%; (○) polymer ligand with percent grafting 172%. [Ligand polymer]: 1.0×10^{-2} mol of iminodiacetic acid L^{-1}. [$CuSO_4$]: 3.0×10^{-3} mol L^{-1}. [H_2O_2]: 2.90×10^{-3} mol L^{-1}. pH: 5.0. Temperature 25°C.

good straight lines are obtained. From the straight lines the pseudo-first-order rate constants, k_1's, were calculated, and tabulated in Table II. Although the hydrogen peroxide is decomposed rather slowly without ligand, the k_1 increases with addition of the polymer ligand, even when the polymer ligand without grafted chain as spacer is used. The increase in k_1 has been presumed to result from the activation of Cu(II) with adsorption by the polymer ligand; in the solution containing a polymer ligand, there is a considerable amount of imperfectly coordinated Cu(II) species, and it has a higher catalytic activity than free Cu(II).[8] Furthermore, it is found that the k_1 increases with addition of polymer ligand in such a way that higher percent grafting gives higher k_1. The value of k_1 for the case with addition of polymer ligand with percent grafting of 172% is about fivefold larger than that for the case with addition of polymer ligand without spacer. These results may be explained by the fact that the amount of coordinated Cu(II) increases with the increasing percent grafting, as shown in A_s in Langmuir's adsorption isotherm, although the catalytic activity of the coordinated Cu(II) itself does not seem to change, at least not so much.

TABLE II
k_1 for Decomposition of Hydrogen Peroxide in the Presence of the Polymer Ligand–Cu(II) Complex, Depending on the Percent Grafting of the Ligand

	Percent grafting (%)				Without ligand
	0	68	123	172	
k_1 (10^{-6} s^{-1})	1.73	4.48	6.53	9.03	0.77

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