

# Studies on Graft Polymerization onto Glass Fibers. II. Graft Copolymerization of Glass Fiber Having Pendent Mercaptan Groups and Its Application

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## Synopsis

Graft polymerization of styrene using a glass fiber having pendent mercaptan groups was carried out under nitrogen in sealed tubes. The percent grafting appeared to increase with monomer concentration, and also to depend to a large extent on the initiator concentration. When CHPO was used as initiator, the percent grafting was maximum at the initiator concentration of 0.02 mol/L. The percent grafting saturation values decreased with increase in the temperature of polymerization. Chain transfer constants and grafting efficiency, both calculated from the equation of Fox et al., were compared with the experimental results. The absorption of Ag ion increased with increase in the percent grafting, and a maximum appeared at a solution pH of 4.0.

## INTRODUCTION

We previously reported that graft copolymerization of styrene, methylmethacrylate, etc., onto a glass fiber at its silanol surface groups introducing an unsaturated group under nitrogen in sealed tubes indicated similar behavior to that of the usual organic fiber with respect to grafting.<sup>1</sup> In addition, it was reported that composite materials obtained from the grafted glass fiber had remarkably improved mechanical properties, particularly interlaminar shear strength.

It is well known that the introduction of mercaptan groups into a polymer molecule increases the chain transfer reactivity of the polymer, and effective graft polymerization is therefore attained.<sup>2-4</sup> In this study, the graft polymerization of styrene monomer on a backbone polymer, a glass fiber into which a mercaptan group is introduced into the silanol group of its surface, has been tried. Also, a thiourea-modified graft glass fiber was prepared, and the absorption behavior of Ag ion in this system was studied.

## EXPERIMENTAL

### Materials

E-Glass fiber of Nitto Boseki Co. was used and submitted to hydrothermal treatment under various conditions. Styrene, glycidyl methacrylate, and 2-mercaptoethanol were first distilled. Thionyl chloride and thiourea were special-grade reagents. Benzoyl peroxide (BPO) was refined by recrystallization,

and cumene hydroperoxide (CHPO) was (special-grade reagent) used without further purification.

### **Preparation of Glass Fiber with Pendent Mercaptan Groups and Grafting Procedure**

E-Glass fiber is treated with hot water at 60 to 100°C for 1 to 5 h, dried under reduced pressure, and then treated in excess thionyl chloride at 100°C for 1 h in a reaction tube by throughing a stream of dry nitrogen. After removing excess thionyl chloride under reduced pressure, an excess of a 2-mercaptoethanol-benzene (1:9) mixture is added to the reaction tube, where the glass fiber is treated at 90 to 100°C for 1 h. Then, excess 2-mercaptoethanol-benzene mixture is removed under reduced pressure. The glass fiber with pendent mercaptan groups thus obtained and various concentrations of benzene solutions of styrene are then put in a polymerization tube together with benzoyl peroxide or cumene hydroperoxide as initiator, and graft polymerization is then carried out at 65 to 90°C under nitrogen in sealed tubes. After grafting, grafted glass fibers were subjected to acetone extraction in a Soxhlet extractor to remove the homopolymers. After drying, the percent grafting and the grafting efficiency were determined according to the preceding report.<sup>1</sup>

### **Preparation of Thiourea-Modified Graft Glass Fiber for Adsorption of Ag Ion**

Graft copolymerization of styrene-glycidyl methacrylate onto glass fiber was carried out with cumene hydroperoxide as a initiator at 80°C in a sealed tube in nitrogen atmosphere, and the thiourea-modified graft glass fiber was prepared by treating the fiber in 5.5% thiourea aqueous solution for 4 h at 80°C.

### **Analysis of Chlorine and Mercaptan Groups**

The determination of chlorine group was made by the method of Yamashita and Kohjiya,<sup>5</sup> and mercaptan group was determined by the methods of Gluckman et al.,<sup>3</sup> Kinhol et al.<sup>6</sup> etc.

### **Viscosity Measurement of Polystyrene Solution**

The intrinsic viscosities  $[\eta]$  were obtained in benzene at  $30 \pm 0.1^\circ\text{C}$  by the use of the Ostwald viscometer. Viscosity-average molecular weight of polystyrene was calculated from the following equation<sup>7</sup>:

$$\log M = 5.222 + 1.37 \log [\eta]$$

### **Measurement Residual Ag Ion Concentration**

The adsorption of Ag ion to the graft glass fiber was determined by atomic absorption spectroscopy (Shimazu AA-610 type).

TABLE I  
Relation Between Mercaptan and Chlorine Groups of Glass Fiber Treated with  
2-Mercaptoethanol

	60°C <sup>a</sup>			100°C		
	1 h <sup>b</sup>	3 h	5 h	0.5 h	1 h	2 h
Chlorine group concn., $\times 10^{-4}$ mol/L	0.92	0.36	0.32	0.68	0.22	0.20
Mercaptan group concn., $\times 10^{-4}$ mol/L	0.75	1.04	1.34	0.96	1.44	1.45

<sup>a</sup> Reaction temperature.

<sup>b</sup> Reaction time.

## RESULTS AND DISCUSSION

### Graft Copolymerization of Glass Fiber Having Pendent Mercaptan Groups

In the various treatments of the glass fiber with 2-mercaptoethanol, mercaptan groups were introduced onto the glass fiber. The results are shown in Table I. With increasing reaction time and temperature, the formation of mercaptan groups was increased owing to the reaction of 2-mercaptoethanol with the chlorine groups of the glass fiber.

Figure 1 shows the effects of monomer concentration on the percent grafting. The percent grafting is increased in proportion to the concentration of monomer and tends to reach the saturated value in later reaction period.

Figure 2 shows the effects of initiator concentration on the percent grafting, which indicates an optimum initiator concentration; that is, the percent grafting reaches a maximum value at an initiator concentration of 0.02 mol/L. A similar tendency has been observed in the graft polymerization of styrene on the mer-

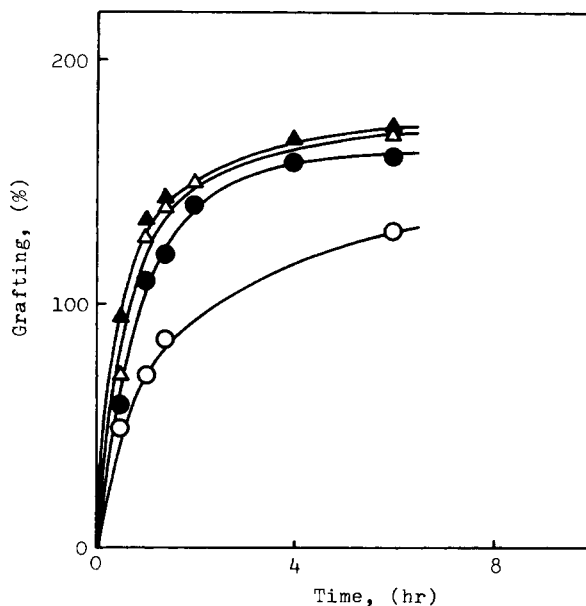


Fig. 1. Effect of monomer concentration on percent grafting.  $[\text{CHPO}] = 0.02$  mol/L,  $[\text{GF}] = 8$  g/L, at 80°C: (○) 5 mol/L; (●) 6 mol/L; (△) 7 mol/L, (▲) 8 mol/L.

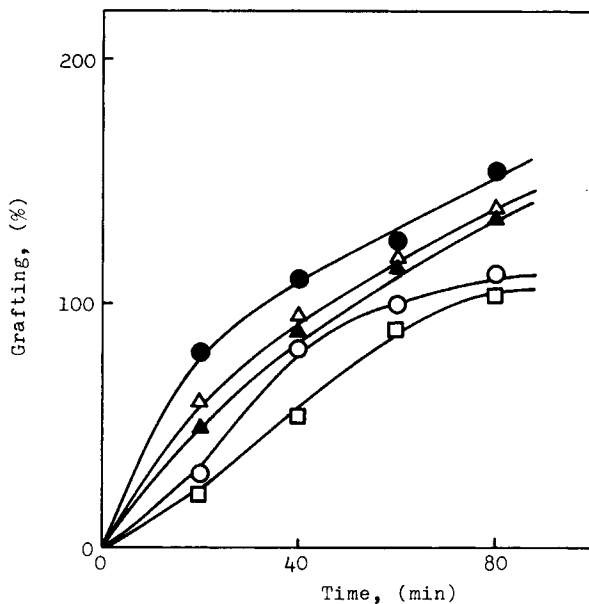


Fig. 2. Influence of initiator concentration on percent grafting.  $[St] = 7 \text{ mol/L}$ ,  $[GF] = 8 \text{ g/L}$ , at  $80^\circ\text{C}$ : (○)  $0.01 \text{ mol/L}$ ; (●)  $0.02 \text{ mol/L}$ ; (△)  $0.04 \text{ mol/L}$ ; (▲)  $0.06 \text{ mol/L}$ ; (□)  $0.08 \text{ mol/L}$ .

captan group-introduced carbon fiber<sup>8</sup> and graft polymerization of methyl methacrylate on cellulose.<sup>9,10</sup> After the grafted glass fibers were immersed in 20% aqueous solution of hydrofluoric acid at  $25^\circ\text{C}$  for 300 h, polystyrene branches were isolated and washed thoroughly with pure water. The molecular weights of the polystyrene branches were determined.

The relationships among the average molecular weights of the polystyrene branches and homopolymer, initiator concentration, and the percent grafting are shown in Table II. Also, the apparent number of branches was obtained by the use of Okamura's formula<sup>11</sup> (Table II). The percent grafting and the apparent number of branches increase to a maximum and then decrease with further increase in the concentration of the initiator. This means that at high initiator concentration, the initiator radicals disappear by reacting with backbone glass fiber radical. Also, in a heterogeneous system such as this experiment, the diffusion of monomer into the fiber creates a gel effect resulting in a higher degree of polymerization for the grafted branches than the homopolymer.

The results in regard to the graft polymerization behavior with the different

TABLE II  
Influence of Initiator Concentration on Percent Grafting, Molecular Weight of Polystyrene Branches, Molecular Weight of Homopolymer, and Apparent Number of Branches

CHPO, mol/L	Percent grafting, %	Polystyrene branches, $\bar{M} \times 10^{-3}$	Homopolymer, $\bar{M} \times 10^{-3}$	Apparent number of branches, $\bar{M} \times 10^{-3}$
0.01	85	1.52	1.36	2.01
0.02	120	1.48	1.32	2.56
0.04	95	1.94	1.49	0.97
0.06	90	2.15	1.96	0.74

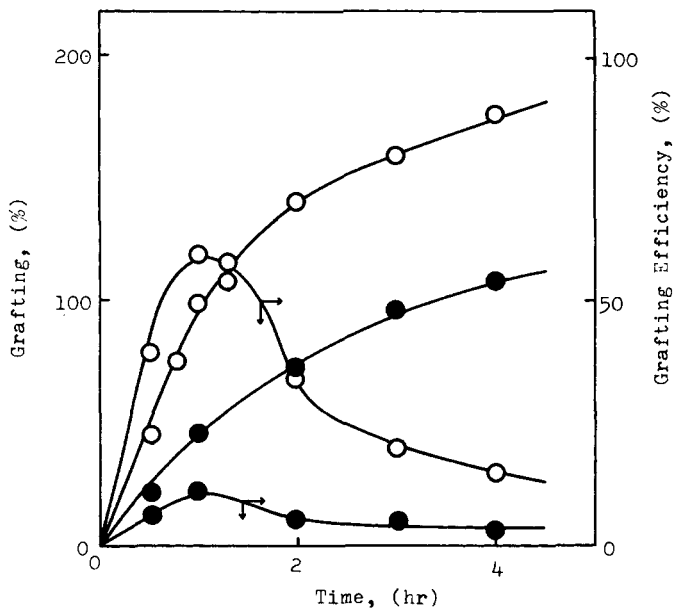


Fig. 3. Effect of initiator on the graft copolymerization.  $[St] = 7 \text{ mol/L}$ ,  $[C] = 0.01 \text{ mol/L}$ ,  $[GF] = 8 \text{ g/L}$ , at  $80^\circ\text{C}$ . Percent grafting: (O) CHPO; (●) BPO. Grafting efficiency: ( $\Delta$ ) CHPO; ( $\blacktriangle$ ) BPO.

initiators are shown in Figure 3. Although the percent grafting appears to increase proportionally to the oxidizing power of initiator in the case of the graft polymerization of polymer with mercaptan groups, the results show that both the percent grafting and the grafting efficiency are greater when using CHPO as an initiator than BPO. This suggests that CHPO is more reactive with mercaptan groups than is BPO.

The chain transfer constant and grafting efficiency are determined theoretically on the basis of kinetic studies by Fox et al.<sup>3,4</sup> The following equations are formulated:

$$\phi = \frac{[SH]}{[SH]_0} = (1 - \alpha)C_s \quad (1)$$

$$\epsilon \cong \left( \frac{1 - \phi}{1 - \phi - y_0 \ln \phi} \right) \left( 1 + \frac{(1 - r)y_0^2}{(\phi + y_0)(1 + y_0)} \right) \quad (2)$$

where  $C_s$  stands for the chain transfer constant,  $\epsilon$  stands for grafting efficiency,  $\alpha$  is the fractional conversion of monomer to polymer,  $[SH]$  is the residual mercaptan content of the polymer at conversion  $\alpha$ ,  $[SH]_0$  is the initiator mercaptan content, and  $r$  is a parameter specifying the fraction of radical-radical termination occurring by disproportionation. Further,  $y_0$  is defined as

$$y_0 = \frac{2(k_t/k_p^2)(d\alpha/dt)_0}{C_s[SH]_0} \quad (3)$$

where  $(d\alpha/dt)_0$  is the initial rate of polymerization expressed in fraction/s and  $k_t/k_p^2$  is the ratio of rate constants for termination and propagation.

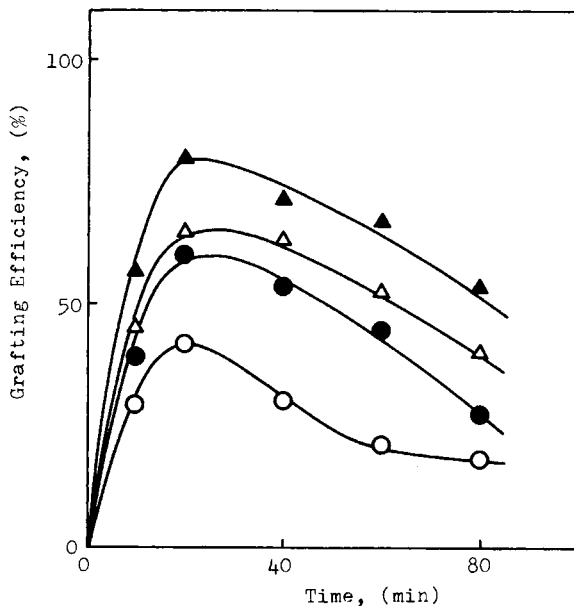


Fig. 4. Relation between glass fiber concentration and grafting efficiency.  $[St] = 7 \text{ mol/L}$ ,  $[CHPO] = 0.02 \text{ mol/L}$ , at  $80^\circ\text{C}$ : (O) 4 g/L; (●) 8 g/L; ( $\Delta$ ) 16 g/L; ( $\blacktriangle$ ) 24 g/L.

Table III shows the calculation results of chain transfer constant  $C_s$  and grafting efficiency  $\epsilon$  obtained according to the method of Fox et al.<sup>3,4</sup>

It is apparent that the chain transfer constant of the mercaptan group-introduced glass fiber varies with the species of initiator and is larger when using CHPO as initiator than BPO. Although the reason is not clear, it seems to be greatly affected by the viscosity of the polymerization system, as stated in the preceding report.<sup>1</sup>

Figure 4 shows the relationship of the concentration of fiber to the grafting efficiency, i.e., the grafting efficiency increases with increasing concentration of fiber, probably because the active grafting points are increased as the fiber concentration increases.

Figure 5 shows the relationship between polymerization temperature and the percent grafting. However, grafting soon reaches a saturation value, especially at high temperatures; the higher the grafting temperature, the smaller the saturation value. Similar results have been observed by Shinohara et al.<sup>12</sup> in the graft copolymerization of *N*-vinyl-2-pyrrolidone. This phenomenon may be caused by either the degradation of the free radicals without contribution to the graft reaction or the shortness of the grafted side chains at high grafting temperature.

Figure 6 shows the relationship between the polymerization temperature and grafting efficiency. Grafting efficiency decreases with increase in the polymerization temperature. From Figures 5 and 6, it is apparent that percent grafting increases with increasing polymerization temperature, while grafting efficiency decreases at the initial stages of graft polymerization. This suggests that the apparent activation energy of the polymerization initiation may be larger than the activation energy of the chain transfer reaction.

Figure 7 gives the relationship between the logarithm of the rate of graft

TABLE III  
Chain Transfer Constants of Polymerization Styrene Monomer with Glass Fiber Having Pendant Mercaptan Groups

Structure of mercaptan	Initiator	Fractional conversion ( $\alpha$ )	[SH]/[SH] <sub>0</sub>	Chain transfer const. ( $C_2$ )	$\epsilon$	
					Calculated	Experimental
GF-O-CH <sub>2</sub> -CH <sub>2</sub> -SH	CHPO	0.02	0.517	32.93	72	68
	BPO	0.08	0.204	10.5	62	56
CF-O-CH <sub>2</sub> -CH <sub>2</sub> -SH <sup>a</sup>	CHPO	0.092	0.182	18.1	89	68
R-OOC-CH <sub>2</sub> -SH <sup>b</sup>		0.069	0.102	32.0	98	58
R-CH(OH)CH <sub>2</sub> -SH <sup>b</sup>		0.111	0.430	7.2	85	79

<sup>a</sup> From A. Tanaka, T. Fujisawa, and R. Yosomiya, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 2267 (1980).

<sup>b</sup> From J. G. Fox, M. S. Gluckmann, F. Gormick, R. K. Graham, and S. Gratch, *J. Polym. Sci.*, **37**, 397 (1959).

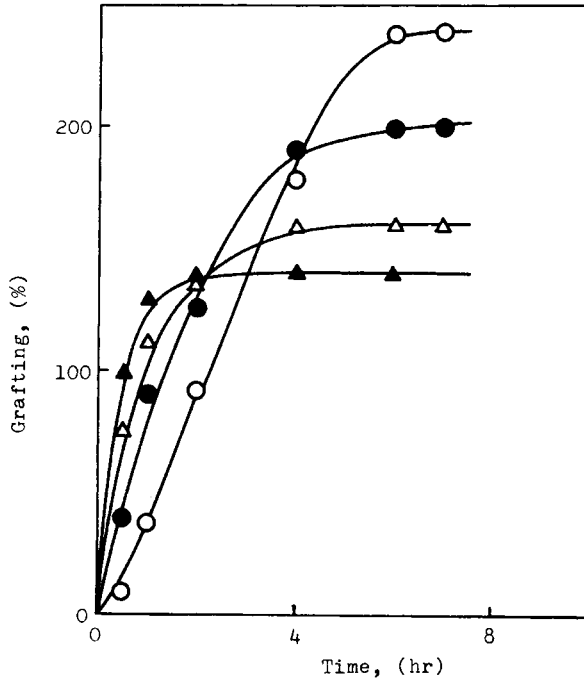


Fig. 5. Effect of grafting temperature in grafting of styrene on glass fiber having pendent mercaptane groups.  $[St] = 7 \text{ mol/L}$ ,  $[CHPO] = 0.02 \text{ mol/L}$ ,  $[GF] = 8 \text{ g/L}$ : (○)  $65^\circ\text{C}$ ; (●)  $70^\circ\text{C}$ ; (△)  $80^\circ\text{C}$ ; (▲)  $90^\circ\text{C}$ .

polymerization and the reciprocal of absolute temperature, showing a nearly linear relation. From the slope of the line, the apparent activation energy is obtained as  $E = 13.7 \text{ kcal/mol}$ . This value, although it is slightly higher than

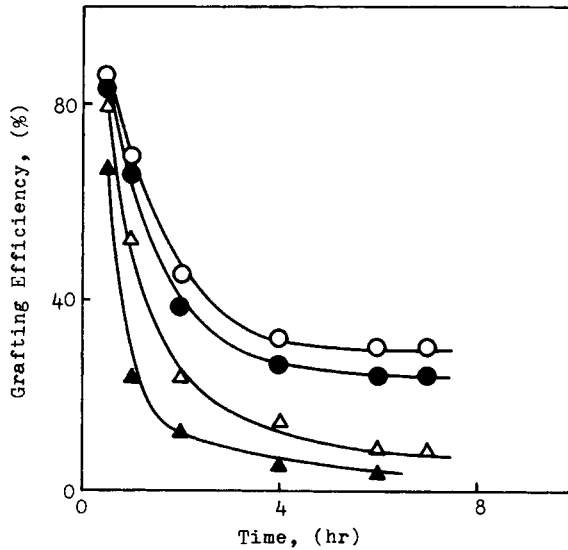


Fig. 6. Effect of grafting temperature on grafting efficiency.  $[St] = 7 \text{ mol/L}$ ,  $[CHPO] = 0.02 \text{ mol/L}$ ,  $[GF] = 8 \text{ g/L}$ : (○)  $65^\circ\text{C}$ ; (●)  $70^\circ\text{C}$ ; (△)  $80^\circ\text{C}$ ; (▲)  $90^\circ\text{C}$ .



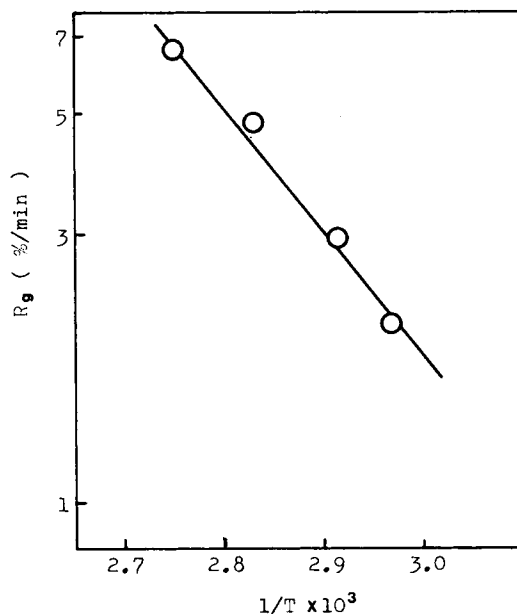


Fig. 7. Rate of graft copolymerization  $R_g$  as function of reciprocal of absolute temperature.

the value for the reaction between monomer and free radical, is considered greatly dependent on the mobility of the polymer radicals and also on the diffusion rate of monomer into the grafted glass fiber on polymerization temperature.

#### Adsorption of Ag Ion to the Thiourea-Modified Graft Glass Fiber

In the batch experiment,  $\text{AgNO}_3$  aqueous solution containing 6 ppm Ag ion was added to 0.5 g of the thiourea-modified graft glass fiber at  $30^\circ\text{C}$ . Relations

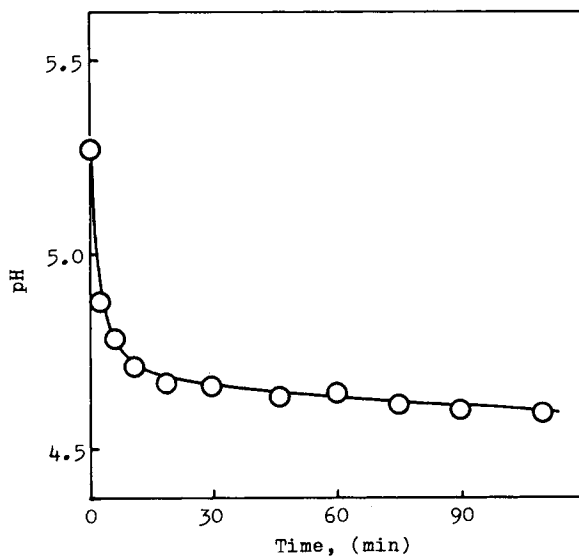
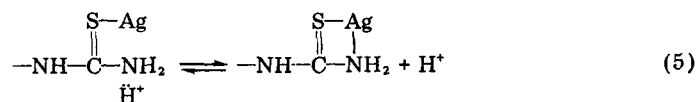
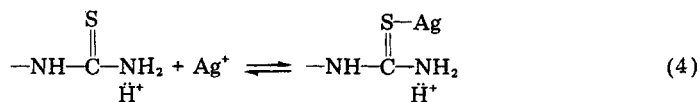


Fig. 8. Reaction time vs. pH behavior of thiourea-modified graft glass fiber at  $30^\circ\text{C}$ .

between pH of  $\text{AgNO}_3$  aqueous solution and reaction time are shown in Figure 8. The pH of the  $\text{AgNO}_3$  aqueous solution decreases with increase in reaction time and achieves complete equilibrium at 2 h. This suggests that the thiourea-modified graft glass fiber adsorbed Ag ions, presumably forming a chelate with them according to the following mechanism<sup>13,14</sup>:



The relationship between adsorption of Ag ion and percent grafting is shown in Figure 9. Adsorption of Ag ion shows a tendency to increase with increasing percent grafting. Also, the difference of monomer composition (St/GMA) at the graft polymerization has a considerable effect on the adsorption of Ag ion, which is maximum at St/GMA = 1/3 (mol ratio).

Figure 10 gives the relationship between the residual Ag ion concentration and adsorbed Ag ion, showing a Freundlich isotherm. Similar results have been observed by Kobayashi et al. for adsorption of Hg ion of thiourea-modified chelate resin.<sup>15,16</sup>

The effect of the pH of  $\text{AgNO}_3$  aqueous solution on adsorption was investigated. The results are shown in Table IV. As can be seen, adsorption of Ag ion by the thiourea-modified graft glass fiber increases to a maximum and then decreases with further increase in pH of the  $\text{AgNO}_3$  aqueous solution.

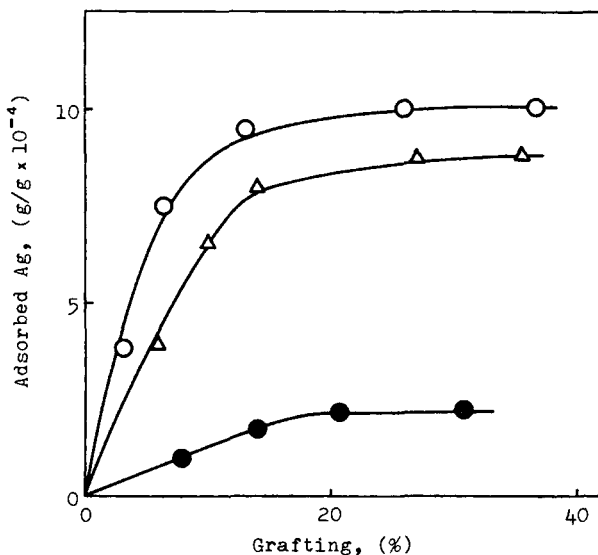


Fig. 9. Relation between Ag adsorption and percent grafting at 40°C. Monomer composition: (○) St/GMA = 1/3; (△) St/GMA = 1/1; (●) St/GMA = 4/1.

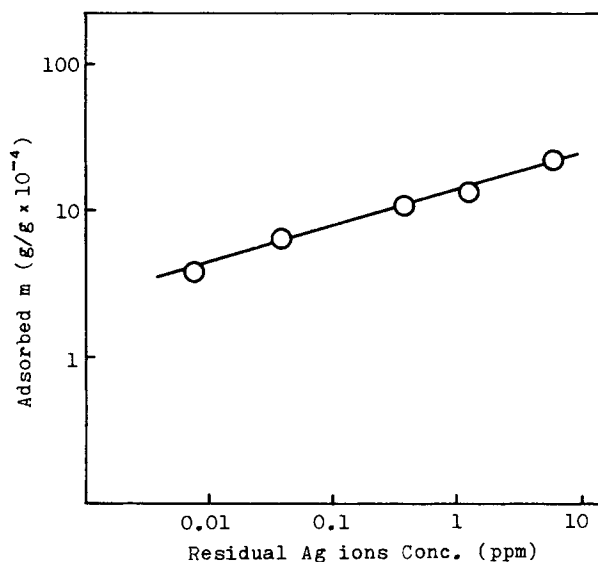


Fig. 10. Adsorption isotherms of thiourea-modified graft glass fiber to Ag ions at 40°C.

TABLE IV  
Adsorption of Ag Ion by Thiourea-Modified Graft Glass Fiber<sup>a</sup>

pH	Adsorbed Ag ion/fiber, (g/g) × 10 <sup>-4</sup>	Adsorption, %
2.0	0.22	2.1
3.1	6.0	56
4.0	10.5	98
5.6	9.7	91
7.0	8.8	82

<sup>a</sup> Initial Ag ion concentration 6 ppm, at 30°C.

Summarizing the adsorption experimental results, the thiourea-modified graft glass fiber has a strong affinity for Ag ions, and this adsorption ability has a large dependence on the composition of the grafted monomer, the percent grafting, and the solution pH.

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