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Grafting of Styrene onto Carbon Fiber Having Perester Groups

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Summary

The oxidized carbon fiber having t-butyl perester groups was prepared by the esterification of acid chloride groups on the carbon fiber with t-butyl hydroperoxide. Then, graft polymerization of styrene onto the carbon fiber having t-butyl perester group was carried out. The concentration of monomer affected grafting efficiency. The grafting efficiency increases with the polymerization time and reachs a constant value above 70°C. Addition of Fe^{2+} and Cu^{2+} to the polymerization system at a concentration of 0.5-1.0 x 10^{-5} mol/l gave the maximum grafting efficiency.

1. Introduction

The introduction of perester groups at random positions on the polymeric backbone substrate to form multifunctional initiator is an important method for graft polymerization. The graft initiating sites are produced by thermal or redox activation of the perester groups. There are several methods of obtaining perester groups along a polymer chain (1-4).

In this study, t-butyl perester group was introduced on the surface of the oxidized carbon fiber. The graft polymerization of styrene onto carbon fiber having t-butyl perester group was tried. Further, the effect of metal ions such as Fe^{2+} and Cu^{2+} upon the graft polymerization was examined.

2. Experimental

2.1 Materials

Acrylonitrile-type carbon fibers (Torayca F-3000 made by Toray Co.) were dipped in tetrahydrofuran at 25°C for 24 hours and dried afterward. Benzene, dioxane, dimethylformamide and dimethylacetamide were purified by distillation of their first grade reagents.

Styrene monomer is of commercial grade. It was washed to remove inhibitor and vacuum-distilled (bp. 55°C 30 mmHg) shortly before use. Thionyl chloride, t-butyl hydroperoxide, $FeSO_4 \cdot 7H_2O$ and $CuCl_2 \cdot 2H_2O$ are of first grade reagents, and were used without purification.

2.2 Preparation of carbon fiber having perester groups, and grafting procedure

Carbon fibers were treated in 20% nitric acide at 100°C for 2 hours, thoroughly washed with water and then dried in vacuum at 50°C for 30 hours.

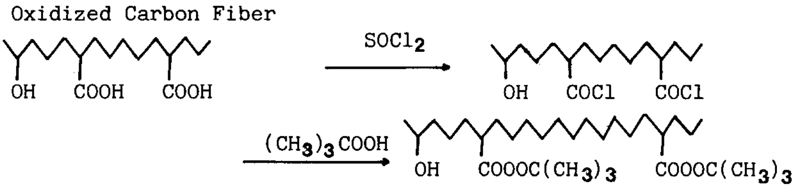
The oxidized carbon fiber was put into reaction tube and treated with excess thionyl chloride in a stream of dry nitrogen at 100°C for 1 hour. After the reaction with thionyl chloride, the residual thionyl chloride was removed under reduced pressure. Then, dioxane containing t-butyl hydroperoxide at a concentration of 5% was put to reaction tube and kept at 25-50°C for 2-6 hours. Furthermore, a little amount of dry pyridine was added in the reaction tube. Carbon fiber having perester groups was washed thoroughly with petroleum ether and dried in vacuum at 20°C for 40 hours.

Graft polymerization of styrene onto the carbon fibers having perester groups was carried out at 60-80°C under nitrogen atmosphere. The homopolymer was removed by acetone in a Soxhlet extractor for 15-30 hours (extraction to a constant weight). After drying in vacuum, grafting percents and grafting efficiency were determined, i.e.,

$$\text{Grafting percent} = \frac{\text{Weight of grafted polymer}}{\text{Weight of carbon fiber}} \times 100$$

$$\text{Graffting efficiency} = \frac{\text{Weight of grafted polymer}}{\text{Weight of grafted polymer} + \text{Weight of homopolyer}} \times 100$$

The scheme of the synthesis is shown below.



2.3 Analysis

Perester group was determined according to Nozaki's method (6). Both -OH and -COOH groups on the oxidized carbon fiber were analyzed according to Boelum's method (7), and the acid chloride group, according to Matuoka's method (8).

The viscosity average molecular weight of polystyrene was estimated by the following equation (9). The intrinsic viscosity (η) was determined in benzene at 30°C by means of an Ostwald's viscosimeter.

$$\log M = 5.222 + 1.37 \log (\eta)$$

3. Results and Discussion

3.1 Peresterification reaction and its decomposition reaction

The result of the reaction of carbon fiber having acid chloride group with t-butyl hydroperoxide is shown in Figure 1. The higher the temperature of the peresterification, the greater becomes the rate of reaction. The content of perester group finally approaches a constant value of 9×10^{-5} mol/g, which is nearly equal to the content of carboxyl group (9.1×10^{-5} mol/g) in the oxidized carbon fiber. The residual -OH, -COOH and -COCl groups present in the carbon fibers having t-butyl perester groups were determined. The result showed that the content of -OH group was 0.68×10^{-5} mol/g which was equal to that in the oxidized carbon fiber before the treatment with thionyl chloride, while -COOH and -COCl groups were hardly detected.

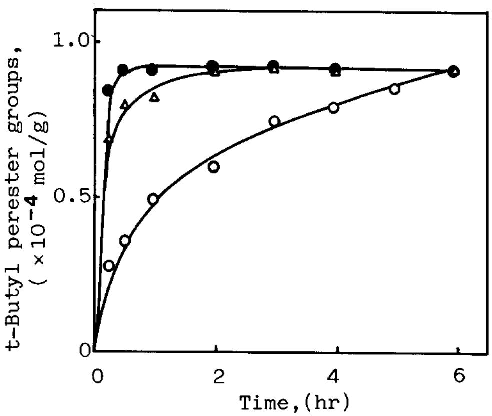


Fig. 1. Amount of t-butyl perester groups on the oxidized carbon fiber by peresterification. (○) 25°C, (△) 40°C, (●) 50°C.

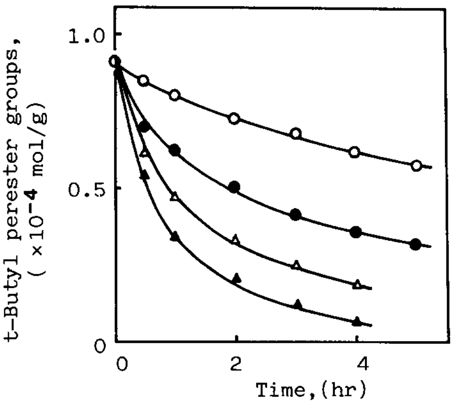


Fig. 2. Thermal decomposition of t-butyl perester groups on the oxidized carbon fiber. (○) 70°C, (●) 80°C, (△) 85°C, (▲) 90°C.

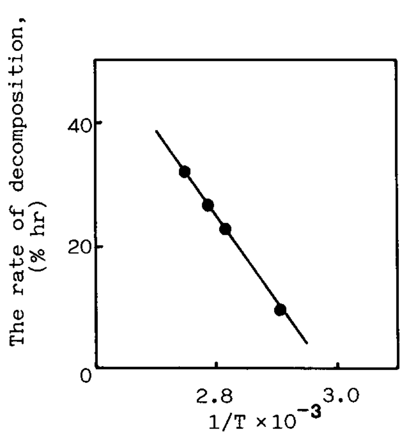


Fig. 3. Relation between the rate of decomposition of t-butyl perester groups and the reciprocal of absolute temperature.

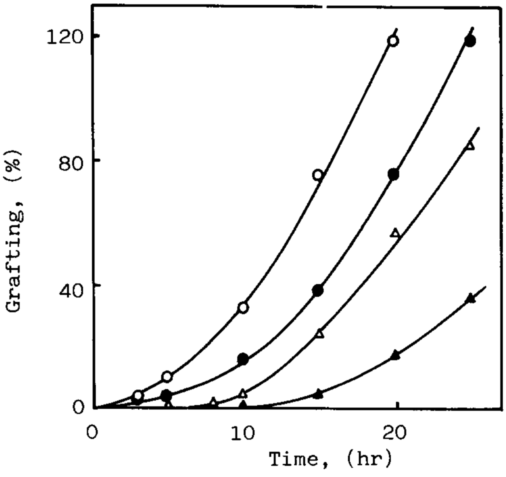


Fig. 4. Effect of monomer concentration [St] on grafting percents at 70°C. [CF] = 20g/l. (▲) 3 mol/l, (△) 4 mol/l, (●) 5 mol/l, (○) 6 mol/l.

Thus the t-butyl perester group introduced onto the surface of carbon fiber was relatively thermally stable and it began to decompose at higher temperatures than 60°C. Now, 1 g of the carbon fibers having t-butyl perester groups was put into 100 ml of dioxane solution, and the decomposition rate of t-butyl perester group was determined at various temperatures above 60°C. The result is shown in Figure 2. The decomposition rate of t-butyl perester groups shows a tendency to increase with increasing temperature. The rate of decomposition was plotted against the reciprocal of absolute temperature in Figure 3, which shows a nearly linear relation.

From the results, the rate of decomposition of t-butyl perester group shows a tendency to increase with increasing temperature.

3.2 Graft polymerization of styrene onto carbon fibers

Graft polymerization of styrene onto carbon fiber having t-butyl perester groups was carried out at 70°C.

The effect of the monomer concentration on the grafting persents is shown in Figure 4. The grafting percents increases with increasing monomer concentration.

The relation between the grafting efficiency and the monomer concentration is shown in Figure 5, which indicates that the grafting efficiency increased with the increase of monomer concentration. The grafting efficiency obtained is much higher than that attained by the chain transfer of mercapto group (10). Moreover, homopolymer is produced a little. The relation between the amount of carbon fiber and the grafting efficiency is shown in Figure 6, which indicates that the grafting efficiency increased with the increase of the amount of carbon fiber (concentration of t-butyl perester group). It was also found that the grafting efficiency increased with polymerization time to reach a constant value. Generally, in the graft polymerization by the chain transfer reaction, the grafting efficiency shows a tendency to decrease, as the concentration of initiator and the polymerization time are increased. Ide et al. (11) reported that the graft polymerization of methyl methacrylate onto urethanized poly(vinyl alcohol) showed the same behavior as mentioned above. It is considered that in the case as shown in Figure 6 an impurity component such as residual phenolic-OH group in carbon fibers (10) which acts as a chain transfer agent or an inhibitor in the polymerization system is consumed at the early stage of the polymerization, so the grafting efficiency increases as the polymerization time becomes longer. The relation between the grafting percents and

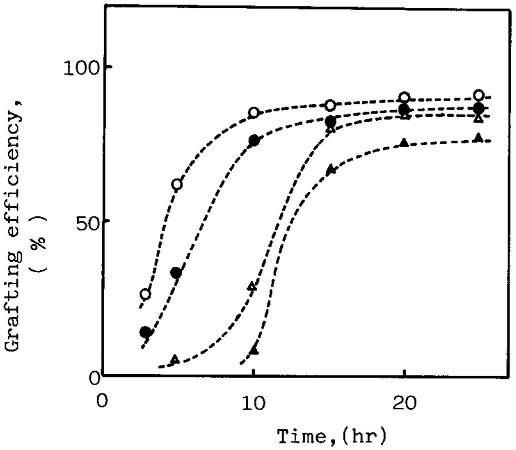


Fig. 5. Effect of monomer concentration [St] on grafting efficiency at 70°C. [CF] = 20 g/l.
(▲) 3 mol/l, (△) 4 mol/l,
(●) 5 mol/l, (○) 6 mol/l.

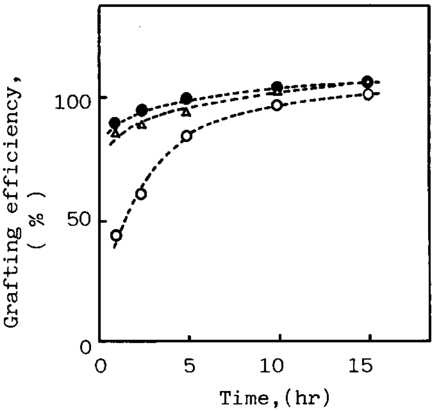


Fig. 6. Effect of the amount of carbon fiber. [CF] on grafting efficiency.
[St] = 6 mol/l, at 70°C.
(○) 10 g/l, (△) 20 g/l,
(●) 30 g/l.

the molecular weight of the homopolymer produced is shown in Table 1. The molecular weight of the homopolymer is much smaller than that given in the previous report (10).

Table 1. Molecular Weights of Homopolymers, Grafting Percents and Grafting Efficiencies.

	Grafting persents (%)	Grafting efficiency (%)	Homopolymer $\bar{P}\times10^{-3}$
[M] = 6 mol/l [CF] = 20 g/l at 70 °C	32.4	86.2	5.2
	75.0	88.0	5.6
	118.8	91.2	5.5
[M] = 6 mol/l [CF] = 20 g/l at 80 °C	14.8	63.8	3.8
	27.0	75.0	3.8
	95.2	88.4	4.0

The effect of solvent (benzene, dioxane, dimethylformamide and dimethylacetamide) on the graft polymerization was also investigated. The result are shown in Table 2. The differences in the overall rates of polymerization for those solvent are not so great, while both the grafting persents and the grafting efficiency decrease in the following order: benzene > dioxane > dimethylformamide > dimethylacetamide. The difference would be due to the difference in the chain transfer reaction of the polymer radical with the solvent molecule, and in fact, the chain transfer constants of the above solvents decrease in the order: dimethylacetamide > dimethylformamide > dioxane > benzene, (12) which suggest that a solvent of higher chain transfer constant depressed more the graft polymerization.

The dependence of the grafting percents and the grafting efficiency upon the polymerization temperature is shown in Figure 7. Both the grafting percents and grafting efficiency show a tendency to increase with increasing polymerization temperature.

Table 2. Influence of Solvent.

Solvent	Total conversion (%)	Grafting percens (%)	Grafting efficiency (%)
Benzene	8.42	68.9	85.4
Dioxane	5.90	46.5	30.8
Dimethylformamide	4.72	29.2	20.5
Dimethylacetamide	4.25	21.0	14.7

[M] = 5 mol/l, [CF] = 20 g/l, Temperature = 70 °C, Time = 20 hr.

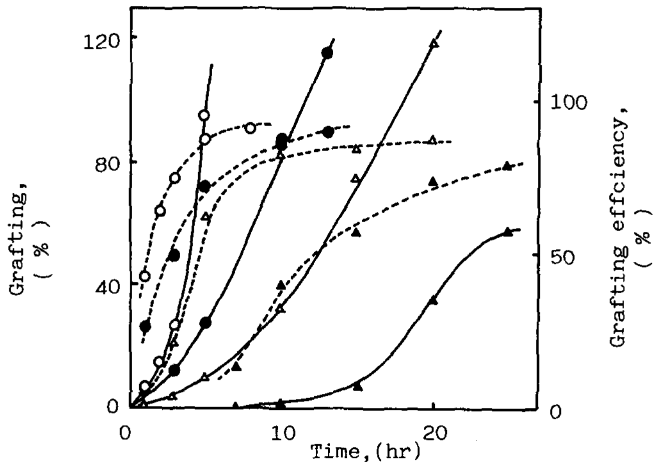


Fig. 7. Effect of polymerization temperature on percent grafting and grafting efficiency.
[St] = 6 mol/l, [CF] = 20 g/l.
(——) Grafting percents,(----) Grafting efficiency.
(▲) 60°C, (△) 70°C, (●) 75°C, (○) 80°C.

3.3 Effect of addition of transition metal salts on graft polymerization

It is well known (13, 14) that the metal ions such as $Fe^{2+}$and Cu^{2+} induce the decomposition of hydroperoxide, and thus affect the polymerization of vinyl monomer. If it is assumed that carbon fibers having perester groups respond to ferrous ion in a similar manner a hydroperoxide, it would be expected that graft polymerization of styrene on the surface of carbon fibers having perester groups should occur effectively.

Figure 8 shows the grafting percents and the grafting efficiency as function of polymerization time in the presence of Fe^{2+} (1×10^{-5}mol/l). The addition of a small amount of Fe^{2+} causes a remarkable increase in both the grafting efficiency and the grafting percents.

The effect of the concentration of Fe^{2+} and Cu^{2+} on the graft polymerization is shown in Figure 9. The grafting percents and the grafting efficiency for both cases of Fe^{2+} and Cu^{2+} show a maximum at approximate $0.5 - 1.0 \times10^{-5}$ mol/l each, and then decrease rapidly as the concentrations of metal ions increase further. El-Azmirly et al. (15) reported the similar behavior on the graft polymerization. It is known (16, 17) that the polymeric peroxide are decomposed at reasonable rates according to the following equation in the presence of ferrous ion, and the graft polymerization will occur as the result of the diffusion of monomer to the macro radicals formed.

$$\text{P-OOH} + Fe^{2+} \longrightarrow \text{PO}\cdot + OH^{-} + Fe^{3+} \qquad (1)$$

$$\text{PO}\cdot + \text{M} \longrightarrow \text{PO-M}\cdot \qquad (2)$$

Where P-OOH and M represent polymeric peroxy species and monomer, respectively.

However, on further increasing of the metal ion concentration, a point will be reached at which reaction (3) will compete with reaction (2).

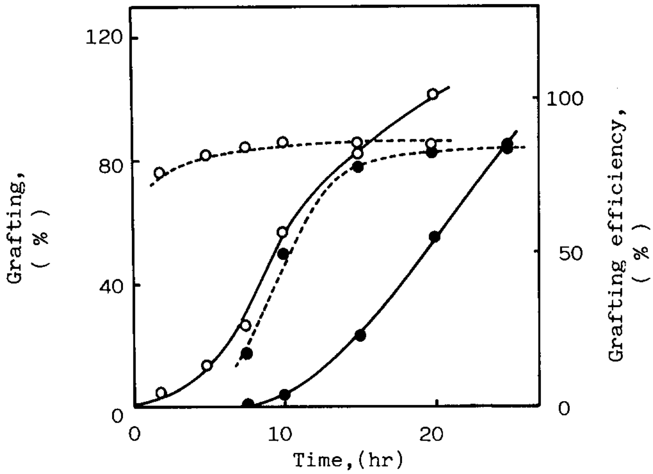


Fig. 8. Additional effect of Fe^{2+} ions on the graft polymerization. [St] = 4 mol/l, [CF] = 20 g/l, at 70°C.
(——) Grafting percents,(----) Grafting efficiency.
(●) No additive, (○) Fe^{+}(1 × 10^{-5}mol/l) additive.

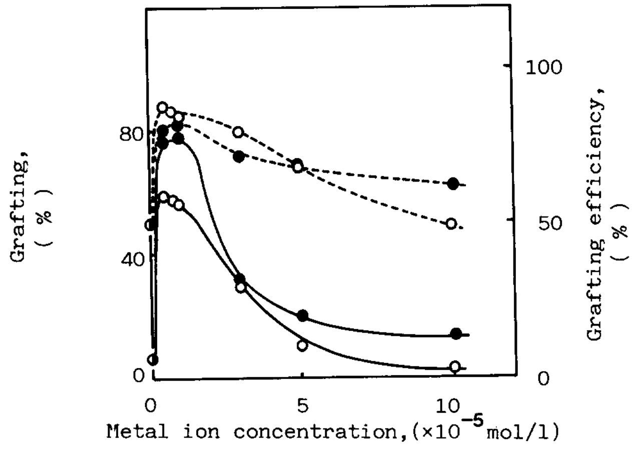
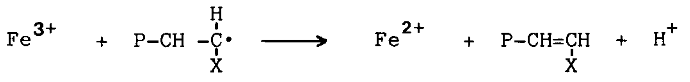


Fig. 9. Influence of metal ions concentration on the graft polymerization. [St] = 4 mol/l, [CF] = 20 g/l, Polymerization time = 1 hr, at 70°C.
(——) Grafting percents,(----) Grafting efficiency.
(○) Fe^{2+}, (●) Cu^{2+}

$$\mathrm{PO}\cdot + \mathrm{Fe}^{2+} \longrightarrow \mathrm{PO}^{-} + \mathrm{Fe}^{3+} \qquad (3)$$

Moreover, as the ferric ions are accumulated, the graft polymerization may be suppressed as a result of termination process that can be represented as; (16, 17)



$$\mathrm{Fe}^{3+} + \mathrm{P{-}CH}{-}\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}}\cdot \longrightarrow \mathrm{Fe}^{2+} + \mathrm{P{-}CH{=}}\underset{\mathrm{X}}{\mathrm{CH}} + \mathrm{H}^{+} \qquad (4)$$

The effect of Cu^{2+} is greater than that Fe^{2+}. It seems that the reaction rate of (1) probably depends upon the redox potential of the metal. The oxidation potential of Cu^{2+} (E°, -0.15V) is higher than that of Fe^{2+} (E°, -0.077V), (18) hence, both the grafting persents and the grafting efficiency in the system including Cu^{2+} are greater than those in the Fe^{2+} system.

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