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Functional Monomers and Polymers. 90.* Radiation-Induced Graft Polymerization of Styrene onto Chitin and Chitosan

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ABSTRACT

The graft polymerization of styrene onto chitin powder, and chitosan powder and film initiated by γ -ray irradiation was carried out at 30°C. The graft polymerization was found to proceed predominantly in the presence of water, and the degree of grafting increased with an increase in the radiation dose. From ESR spectroscopy it was noted that the free radicals generated both in chitin and in chitosan were stable enough at ambient temperature. Styrene-grafted chitin and chitosan powders thus obtained showed less swelling in water, and chitosan after graft polymerization was insoluble in dilute acids. Graft polymerization of other vinyl monomers was also studied.

INTRODUCTION

Chitin is a naturally occurring polysaccharide found in crustaceans, insects, and in the cell walls of bacteria. It is a long, unbranched polysaccharide like cellulose, with an aminoacetyl group instead of a

*For Part 89 of this series, see K. Hanabusa, H. Shirai, N. Hojo, K. Kondo, and K. Takemoto, *Makromol. Chem.*, In Press.

hydroxyl group of the C-2 carbon. Studies on chitin chemistry, however, have hitherto been limited because of its poor solubility and intractability, which are due to a strong micelle structure through hydrogen bonding between aminoacetyl groups.

On the other hand, chitosan, the acid-soluble deacetylated derivative of chitin, can be easily obtained from chitin by hydrolysis. Because of the presence of free amino groups, chitosan demonstrates higher chelation ability to various sorts of metal ions [1, 2] and adsorption ability for halogens such as iodine [3, 4] and bromine [5]. Recently, numerous works were reported for the effective utilization of chitin and chitosan, e.g., on chitin or related polysaccharide gels [6], solvent research for chitin [7], preparation of chitin derivatives [8], and the effect of deacetylation on the properties of chitin [9].

Graft copolymerization onto cellulose has been extensively studied, while very few works on the graft copolymerization onto chitin and chitosan seem to have been reported. Slagel and co-workers received a patent for making paper products with improved dry strength by grafting on chitosan [10]. Kojima and co-workers reported recently the graft copolymerization of methyl methacrylate onto chitin using tributylborane as an initiator [11].

EXPERIMENTAL

Materials

Chitin (N 6.80%, 100-200 mesh) and chitosan (N 8.15%, 100-200 mesh, viscosity 440 cP in 0.5% of 0.25 N acetic acid solution at 20°C) were supplied from Nippon Tennen Gas Kogyo Co. According to the procedure shown in the literature [14], both chitin and chitosan powders were extracted in a Soxhlet extractor with methanol, water, petroleum ether, and acetone in that order, each for about 24 h. Chitosan film was prepared by pouring an aqueous acetic acid solution of chitosan on a clean glass plate maintained at about 60°C, followed by immersing it in a 10% aqueous sodium hydroxide solution [12] (20 μ m in thickness). Styrene and other monomers were purified by the usual methods.

Graft Copolymerization

To 0.30 g portions of thoroughly dried chitin or chitosan were added 10 mL of styrene solution. The glass tubes containing the trunk polymer, monomer, and solvent were evacuated by the freeze and thaw technique, sealed, and maintained in liquid N₂ and exposed to γ -ray from a ⁶⁰Co source with a dose rate of 0.25 Mrd/h. After polymerization at 30°C, the reaction mixture was poured into a large amount of methanol to separate the styrene monomer. The resultant precipitate

was filtered off and extracted with benzene in a Soxhlet apparatus until no more extractable polystyrene remained. The degree of grafting, DG, and the graft efficiency, Eg, were calculated from the following equations:

$$DG(\%) = \frac{\text{weight of grafted polystyrene}}{\text{weight of trunk chitin or chitosan}} \times 100 \quad (1)$$

$$Eg(\%) = \frac{\text{weight of grafted polystyrene}}{\text{weight of grafted polystyrene} + \text{weight of homopolystyrene}} \times 100 \quad (2)$$

ESR Spectra

The ESR spectra were measured for the chitin and chitosan samples in sealed quartz tubes in vacuum by using Model JES-ME2X (Japan Electron Optics Lab. Co.). The sealed tubes for the measurement were maintained in liquid N₂ and exposed to γ -ray with a total dose of 1.0 Mrd.

RESULTS AND DISCUSSION

Study on Free Radicals by ESR Spectroscopy

ESR studies of chitin and chitosan have been recently reported [13, 14]. Muzzarelli and co-workers have shown singlet ESR signals for both chitin and chitosan samples which changed by the action of atmospheric oxygen or that generated from hydrogen peroxide, or by treating with hot water. The observed ESR spectra for chitin and chitosan in our cases were similar to those shown by Muzzarelli and co-workers (Figs. 1a and 2a). On the other hand, the spectra after γ -ray irradiation showed an increase in intensity as shown in Figs. 1b and 2b, and new absorption bands appeared. These spectra suggest that several different kinds of free radicals were produced in chitin and chitosan after γ -ray irradiation. The effect of heating is shown in Fig. 3. It was further shown that the intensities of the resulting spectra appear not to be much affected by keeping the samples at ambient temperature for 20 h and did not drop sharply after heating.

In order to see whether these free radicals generated by the irradiation could initiate graft polymerization, polymerization was undertaken in the presence of styrene monomer as shown in the following section.

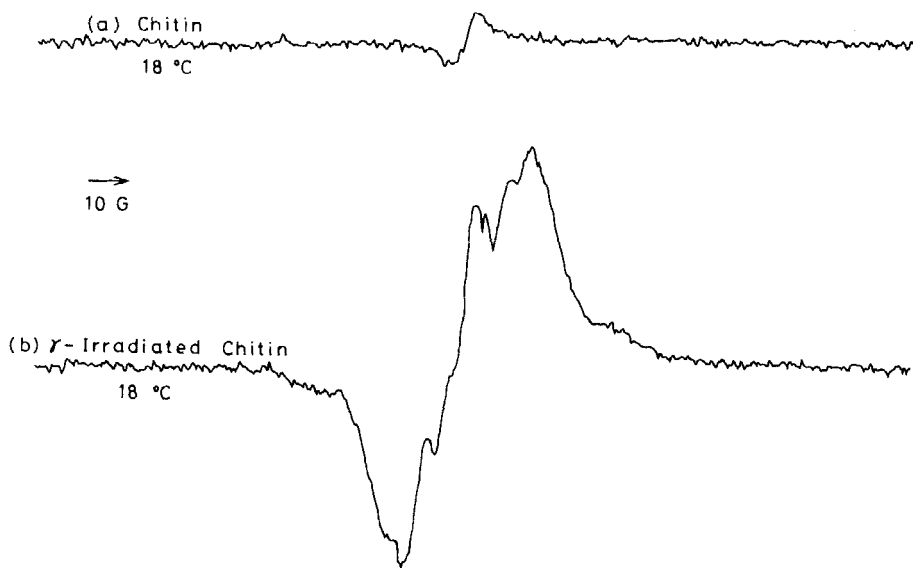


FIG. 1. ESR spectra of chitin samples at 18°C: (a) chitin, (b) γ -ray irradiated chitin.

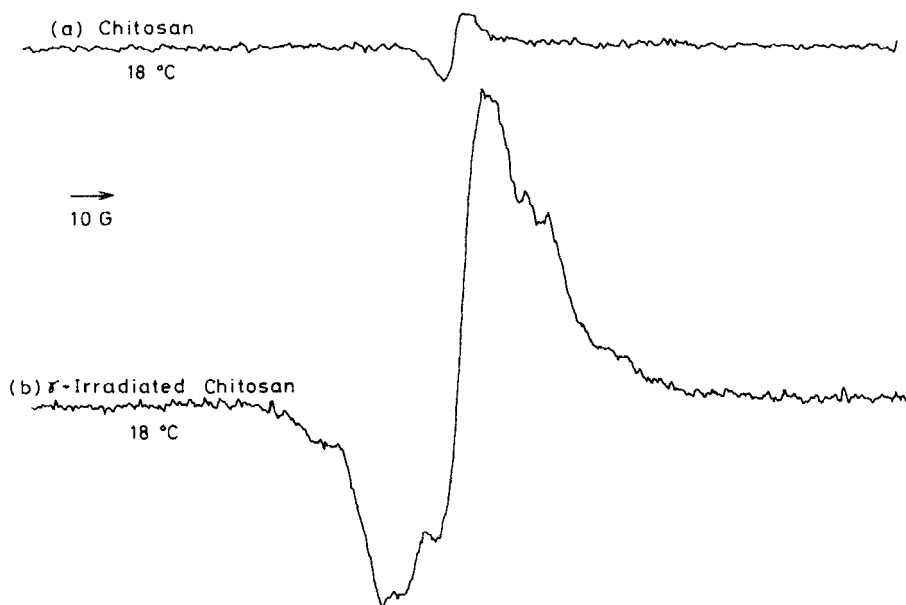


FIG. 2. ESR spectra of chitosan samples at 18°C: (a) chitosan, (b) γ -ray irradiated chitosan.

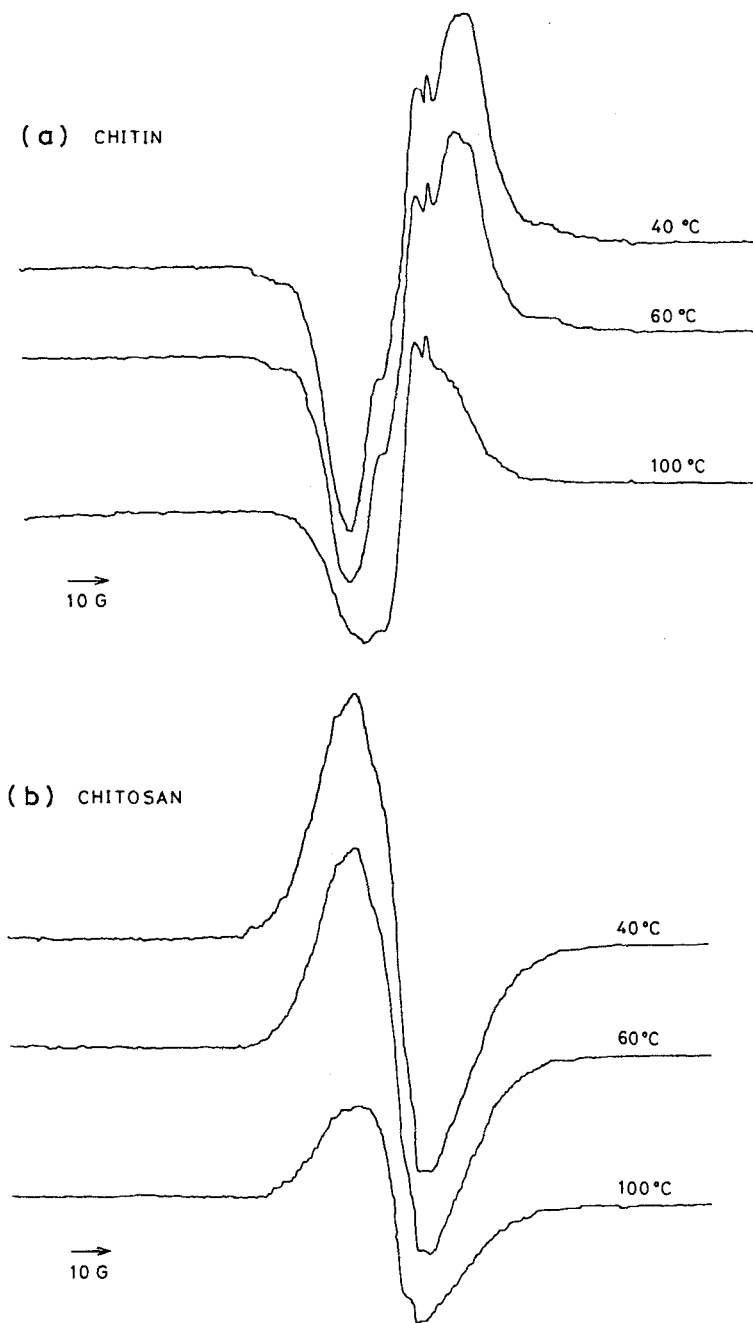


FIG. 3. Effect of heating on free radical concentration ESR spectra after heating (a) irradiated chitin and (b) irradiated chitosan for 5 min at each temperature.

TABLE 1. Grafting of Styrene onto Chitin Powder^a

Monomer and solvent mixture (vol %) ^b	Total conversion (%)	Degree of grafting (DG)	Graft efficiency (Eg) (%)
100 S	3.20	53.4	55.5
50 S-50MeOH	0.06	0	0
50 S-30MeOH-20H ₂ O	0.02	0	0
50 S-50DMF	0.02	0	0
50 S-30DMF-20H ₂ O	1.04	0	0
50 S-50H ₂ O	6.53	63.7	65.4
50 S-50H ₂ O ^c	0.54	0	0
50 S-50H ₂ O ^{c,d}	0.27	-	-

^aTotal polymerization mixture volume, 10 mL; chitin, 0.30 g; temperature, 30°C; time, 48 h; total dose, 0.88 Mrd (0.25 Mrd/h 3.5 h).

^bS, MeOH, and DMF denote styrene, methanol, and dimethylformamide, respectively.

^cNo irradiation.

^dAbsence of chitin.

Grafting of Styrene onto Chitin

Table 1 shows the effect of solvents on grafting of styrene onto chitin powder. Such grafting was found to occur only in the cases when the reaction was performed in bulk or the styrene-water system. In the latter case the degree of grafting was substantially high. It was found that the formation of homopolystyrene was slight in other runs. These results indicate the importance of water for the grafting of styrene onto chitin. A similar result has been reported for tributylboran-initiated grafting of methyl methacrylate onto chitin [11]. Chitin is known to have a crystalline structure, and the molecular chains of chitin are well arranged in piles or sheets linked by hydrogen bonding through amide groups. In the grafting onto chitin, it appears, therefore, that the presence of water would be responsible for the rupture of intermolecular hydrogen bonds between chitin molecules so that styrene molecules can diffuse readily into them.

Grafting of Styrene onto Chitosan

Table 2 shows the effect of solvents on the graft polymerization of styrene onto chitosan powder. Graft polymer could not be obtained

TABLE 2. Grafting of Styrene onto Chitosan Powder^a

Monomer and solvent mixture (vol %)	Total conversion (%)	DG (%)	E _g (%)
100S	0.94	0	0
50S-50MeOH	0.92	7.1	51.5
50S-30MeOH-20H ₂ O	1.07	0	0
50S-50DMF	0.78	0	0
50S-30DMF-20H ₂ O	1.63	0	0
50S-50H ₂ O	7.68	76.1	65.7
50S-50H ₂ O ^b	0.45	0	0
50S-50H ₂ O ^{b,c}	0.27	-	-

^aTotal dose: 1.0 Mrd (0.25 Mrd/h × 4 h).

^bNo irradiation.

^cAbsence of chitosan.

TABLE 3. Grafting of Styrene onto Chitosan Film^a

Monomer and solvent mixture (vol %)	Total conversion (%)	DG (%)	E _g (%)
50S-50Benzene	0.14	0	0
50S-50MeOH	0.54	7.7	94.4
50S-30MeOH-20H ₂ O	2.20	18.3	55.2
50S-50DMF	0.23	0	0
50S-30DMF-20H ₂ O	2.63	8.2	22.0
100S	0.73	5.2	22.3
100S ^b	1.48	37.0	73.3

^aTotal dose: 1.0 Mrd (0.25 Mrd/h × 4 h); thickness of the film: 20 μm.

^bThe chitosan film used was treated previously with water.

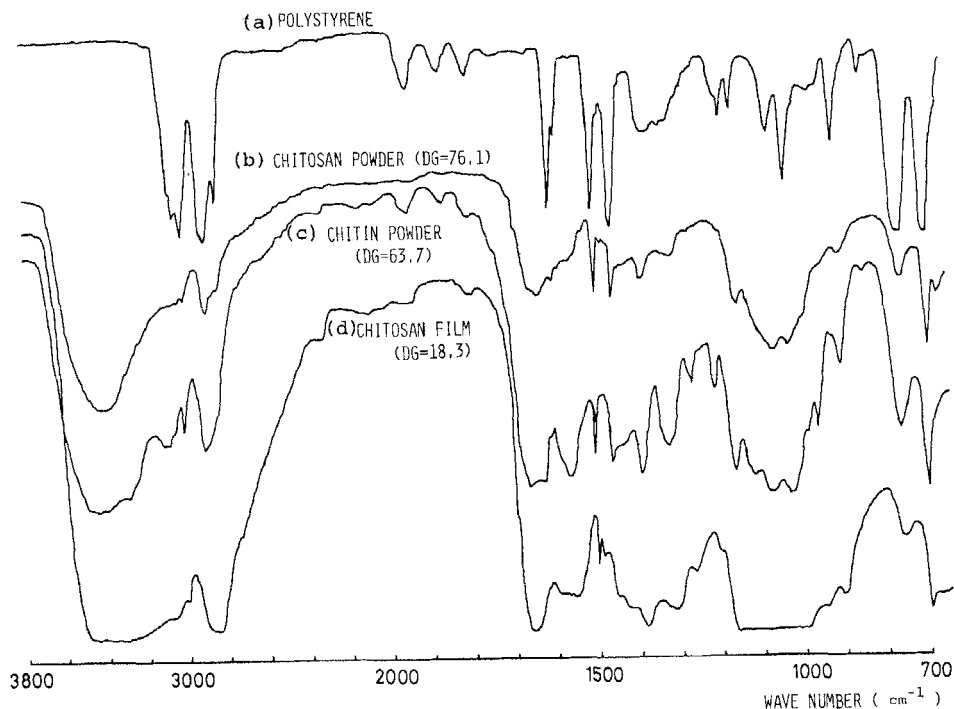


FIG. 4. Infrared spectra of polystyrene-chitin or chitosan graft copolymers: (a) polystyrene, (b) grafted chitosan powder, (c) grafted chitin powder, (d) grafted chitosan film.

in the absence of the solvents. On the other hand, in the case of the reaction in the presence of methanol, a low degree of grafting was reached, though the homopolymer of styrene was formed in trace amount. In the presence of water in the system, a high degree of grafting was attained, which can also be explained by easier diffusion of styrene monomer into the swelled chitosan. Similar runs without irradiation showed no grafting, forming homopolystyrene in only a trace amount.

Table 3 shows the results of grafting of styrene onto chitosan film. The graft polymerization of styrene occurred in methanol, though the degree of grafting was low. It is to be noted that, when the graft polymerization was carried out in styrene monomer after immersing the chitosan film in water, a high degree of grafting was realized. The grafted chitosan film thus obtained (DG = 37%) tends to show less swelling and better elongation intensity in water. From the results it is evident that the difference in the physical structure of chitosan

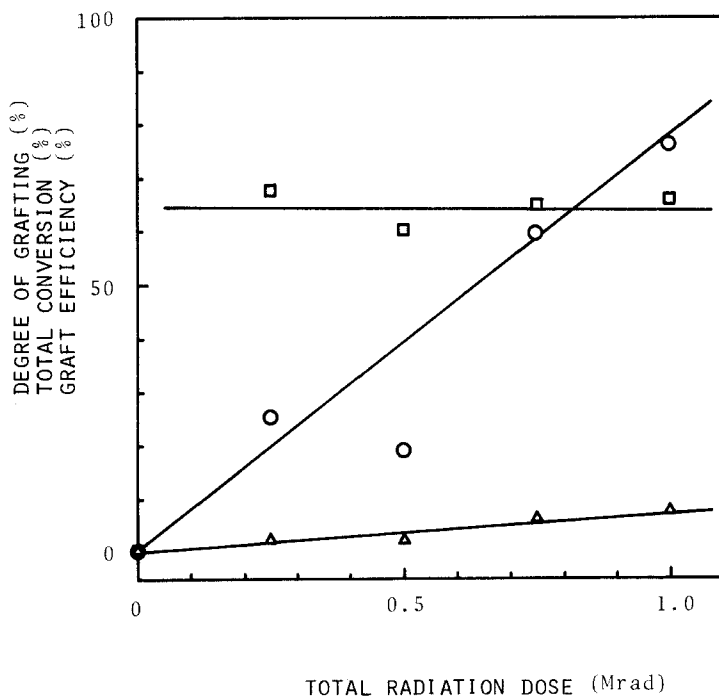


FIG. 5. Effect of radiation dose on grafting onto the chitosan powder. Grafting conditions: chitosan, 0.30 g; styrene, 5 mL; water, 5 mL; temperature, 30°C; time, 48 h. (○) Degree of grafting, (△) total conversion, (□) graft efficiency.

affects the grafting behavior. The IR spectra of the graft polymers are shown in Fig. 4.

Figure 5 shows the effect of radiation dose on grafting onto chitosan powder. The degree of grafting and the total conversion in a 50% styrene/water system tended to increase almost linearly with an increase in the radiation dose in the dose range studied here, while the graft efficiency remained almost constant. Therefore, it seems that the number of activated sites on chitosan should increase in proportion to the radiation dose. Figure 6 shows the influence of reaction time on the degree of grafting onto chitosan powder, total conversion, and graft efficiency. The degree of grafting and the total conversion were found to increase almost linearly with an increase of time. On the other hand, the graft efficiency decreased slightly with a decrease of time, and it seems that the reaction time affects the rate of homopolymerization rather than the rate of grafting.

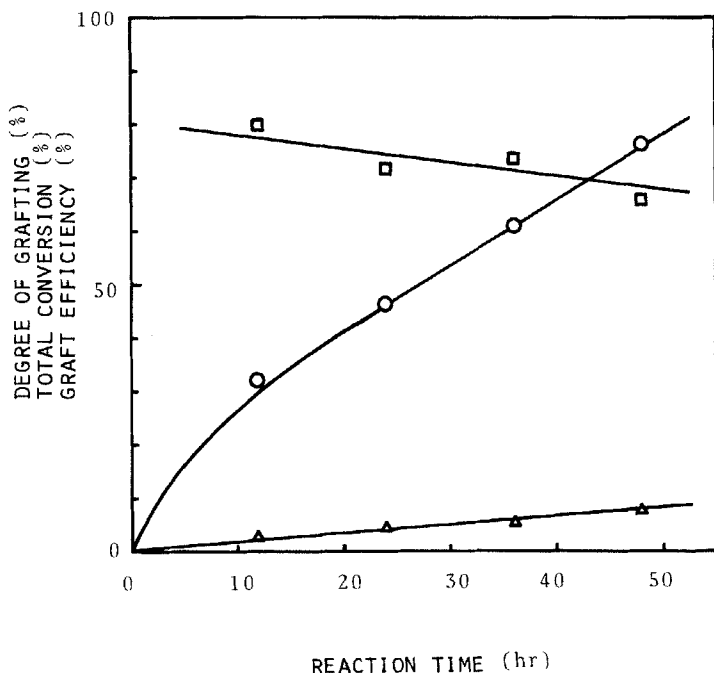


FIG. 6. Effect of reaction time on grafting onto the chitosan powder. Grafting conditions: chitosan, 0.30 g; styrene, 5 mL; water, 5 mL; temperature, 30°C; total dose, 1.0 Mrd. (○) Degree of grafting, (△) total conversion, (□) graft efficiency.

Effects of Water on the Graft Polymerization of Styrene

Figure 7 shows the effect of water content on the graft polymerization of styrene onto chitin powder. It is obvious that the degree of grafting and the total conversion increased in proportion to the increase in water content. It seems that the high water content would make styrene diffusible into the swelled chitin powder. Styrene-grafted chitin thus obtained was a white powder and showed a low tendency to swell with water. The highly grafted chitin was similar to polystyrene.

The effect of water content on grafting onto chitosan powder was examined (Fig. 8). In the case of chitosan, the degree of grafting increased with increasing water content, and it reached about 100%. It was also found, however, that a trace amount of water was necessary for graft polymerization in the case of chitosan, which differed markedly from that of chitin.

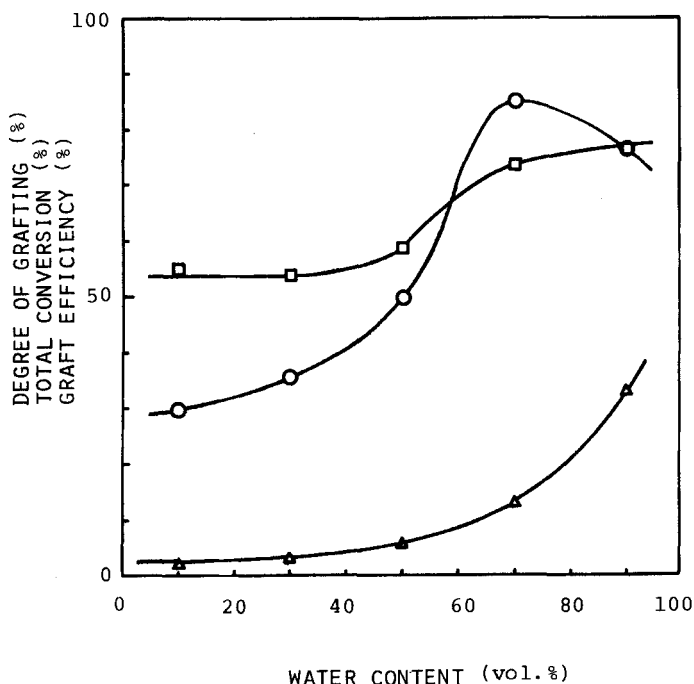


FIG. 7. Effect of styrene concentration on grafting onto the chitin powder. Grafting conditions: chitin, 0.30 g; temperature, 30°C; time, 48 h; total dose, 1.0 Mrd; styrene + water, 10 mL. (○) Degree of grafting, (△) total conversion, (□) graft efficiency.

The graft polymer of chitosan was a colorless powder which showed low swelling to water and had characteristics similar to polystyrene. In general, chitosan dissolves in diluted acids, while the styrene-grafted chitosan derivatives are insoluble in them. For example, styrene-grafted chitosan having more than a 7.0% of degree of grafting is insoluble in 0.25 N acetic acid at room temperature. On the other hand, in the case of styrene-grafted chitosan film, a 7.7% of degree of grafting of styrene does not make chitosan insoluble, and even 37% grafting permits swelling. It appears that such a difference of solubility in the diluted acid comes from their forms; powder or film.

The graft polymerization of other monomers onto chitosan powder is shown in Table 4. Vinyl acetate was found to give no grafted polymer in the condition used. In the case of acrylamide, gelation of the reaction system took place during the polymerization, so that the isolation of the grafted chitosan was difficult. On the other hand,

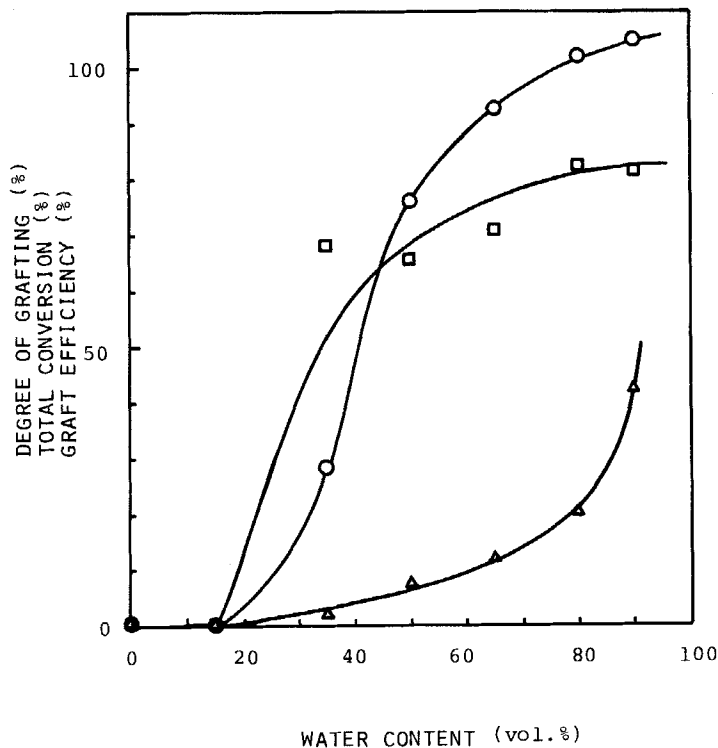


FIG. 8. Effect of styrene concentration on grafting onto the chitosan powder. Grafting conditions: chitosan, 0.30 g; temperature, 30°C; time, 48 h; total dose, 1.0 Mrd; styrene + water, 10 mL. (○) Degree of grafting, (△) total conversion, (□) graft efficiency.

TABLE 4. Grafting of Vinyl Monomers onto the Chitosan Powder by γ -Ray Irradiation^a

Monomer	Total conversion (%)	DG (%)	Eg (%)
Vinyl acetate	0.44	0	0
Acrylamide ^b	45.0	- ^c	- ^c
Methyl methacrylate	71.8	942	84.0
Methyl methacrylate ^d	1.37	10.0	46.8

^aTotal polymerization mixture volume: 10 mL (chitosan: 0.30 g; monomer: 5 mL; water: 5 mL); temperature: 30°C; time: 48 h; total dose: 1.0 Mrd.

^bAcrylamide: 1.50 g; water: 10 mL.

^cThe gelation took place during polymerization.

^dNo irradiation.

methyl methacrylate showed an extremely high degree of grafting, giving the colorless, grafted chitosan powder. Methyl Methacrylate showed a 10% degree of grafting in the absence of γ -ray irradiation, and this grafting seems to be caused by the so-called "no-catalyst polymerization."

Studies on the properties and applications of grafted chitin and chitosans are now in progress.

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