

Synthesis of Deoxy(thiosulfato)chitin as the Precursor for Noncatalytic Photoinduced Graft Copolymerization

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ABSTRACT: Photoinduced graft copolymerization of vinyl monomers onto deoxy(thiosulfato)chitin (S_2O_3 -chitin) has been studied. Chitin was first tosylated and subsequently transformed into S_2O_3 -chitin. S_2O_3 -chitin has good solubility over tosyl-chitin. Graft copolymerization of S_2O_3 -chitin proceeded very easily by ultraviolet irradiation without catalyst. Photolysis of S_2O_3 groups was confirmed by infrared spectra. But the photolysis occurred only in quartz, not in a Pyrex tube. Methyl methacrylate (MMA) and acrylonitrile showed good grafting activities. In the case of acrylic acid and acryl amide, homopolymer formation was predominant, and the degree of grafting was low. We chose the MMA monomer for further information. The grafting rate of S_2O_3 -chitin using MMA was much faster than those of chitin and *O*-acetyl-chitin. Under the appropriate conditions, the degree of grafting reached 600% only in 2 h, and the grafting efficiency was over 75% in any monomer concentration. But addition of DMSO into the polymerization system decreased the degree of grafting. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 71: 189–195, 1999

Key words: chitin; graft copolymerization; deoxy(thiosulfato)chitin; methyl methacrylate; tosyl-chitin

INTRODUCTION

Chitin is a natural polysaccharide that has a similar structure to that of cellulose and is produced in large quantities.¹ Despite much recent research into its utilization, its tightly intermolecular hydrogen bonding and poor solubility to common organic solvents have so far prevented widespread utilization of chitin.

The preparation of tosyl-chitin in lithium chloride-*N,N*-dimethylacetamide (LiCl-DMAc) solvent was previously reported.² As a reactive precursor, this chitin derivative has excellent solubility and reactivity and has the possibility for a wide range of chemical modifications. Chitin derivatives containing the SCN groups can be obtained very easily from tosyl-chitin, whereas this reaction is difficult with untreated chitin.²

Graft copolymerization is an industrially important method. Graft copolymers of chitin are also expected to be novel functional materials. Various methods to improve grafting efficiency, such as the radiation-induced method³ and the initiator method⁴ have been attempted. From series of studies, we have reported that cellulose derivatives containing photodegradable groups, such as carbonyl groups⁵ and acetyl groups,⁶ show high degrees of grafting under moderate reaction conditions.

The grafting reactivity of unmodified chitin is quite low,⁷ but photoinduced graft copolymerization of *O*-acetyl-chitin proceeds very smoothly without catalyst.⁸

For the above reasons, S_2O_3 -chitin, including S-S groups, was prepared by reacting tosyl-chitin with potassium thiosulfate. Then photoinduced graft copolymerization of vinyl monomers onto it was investigated. At the same time, various factors, such as degree of substitution, reac-

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tion time, and solvent concentration on this reaction, were studied.

EXPERIMENTAL

Sample and Reagents

A chitin sample purchased from Tokyo-Kasei was powdered into 50 mesh and purified by extracting with methanol at 50°C for 15 h.⁷ The degree of deacetylation was 0.04, as determined by elemental analysis (anal calc: C, 42.71; H, 6.00; N, 6.28. Found C, 42.65; H, 6.00; N 6.28).

Monomers such as methyl methacrylate (MMA), styrene (St), and acrylic acid (AA) were distilled at reduced pressure, and acrylonitrile (AN) was distilled at atmospheric pressure under nitrogen using a Widmer distillation apparatus. Acrylamide (AAm) was used after recrystallization from benzene. Other reagent grade chemicals were used without further purification.

Synthesis of Deoxy(thiosulfato)chitin (S₂O₃-Chitin)

Tosyl-chitin was prepared according to the previous article.² Tosyl-chitin (3.9 g, 4.92×10^{-3} mol of pyranose unit) was dissolved in dimethylsulfoxide (DMSO) (200 mL) with stirring in a nitrogen atmosphere at 70°C for 20 min. Then sodium thiosulfate (46.7 g, 2.95×10^{-1} mol) was added into this solution, and the reaction was carried out with stirring at 75°C for 24 h. The product was precipitated in a large amount of cold acetone. The precipitate was dialyzed for 48 h in running pure water to remove unreacted reagent and then freeze-dried (DS 0.47. Anal calc: C, 36.69; H, 4.93; N, 5.35. found: C, 37.37; H, 5.63; N, 5.35).

Graft Copolymerization

Powdered S₂O₃-chitin (40-mesh pass) was weighed into a quartz and a Pyrex tube (15 mm in diameter and 110 mm long). To these samples were added water, solvent, and monomer (12 mL total volume). The tubes were sealed after a flush with nitrogen gas. The polymerization was carried out at 50°C for a fixed time in a rotary photo chemical reactor (Riko RH400-10W) by irradiating with ultraviolet (UV) light with a 160-W low-pressure mercury lamp (Model No. UVL-10LA) at distance of 75 mm. Polymerization was terminated by adding a few drops of a saturated aqueous hydroquinone solution. The polymerized mixture was precipitated in a large amount of precipitant and left overnight. Ho-

mopolymer was extracted thoroughly acetone for poly(methyl methacrylate) (PMMA), with benzene for pSt, with DMF for PAN and with water for PAA and PAAM. The remaining product was considered to be a graft copolymer. The yield of polymer was calculated from the following equations.

Total conversion (%)

$$= \frac{\text{Total weight of polymerized MMA}}{\text{Initial MMA weight}} \times 100$$

$$\text{Grafting (\%)} = \frac{\text{Weight of grafted PMMA}}{\text{Weight of S}_2\text{O}_3\text{-chitin}} \times 100$$

Grafting efficiency (%)

$$= \frac{\text{Weight of grafted PMMA}}{\text{Total weight of polymerized MMA}} \times 100$$

Isolation of Grafted Chains and Measurement of Molecular Weight⁹

Hydrolysis of trunk polymer was carried out by adding 50 mL of 20*N* sulfuric acid to 0.15 g of graft copolymer at 60°C for 30 min. The solution was cooled, diluted with 600 mL of water, and allowed to stand at 25°C for 12 h. Then it was filtered and washed with water until it was free of acid using methyl orange as indicator. The residue (crude PMMA) was dissolved in acetone and purified by reprecipitation with methanol. The obtained PMMA was dissolved in benzene, and the intrinsic viscosity was measured. From the results, the molecular weight was calculated by the following equation¹⁰:

$$\log \overline{Pn} = 3.346 + 1.32 \log[\eta], 30^\circ\text{C, benzene}$$

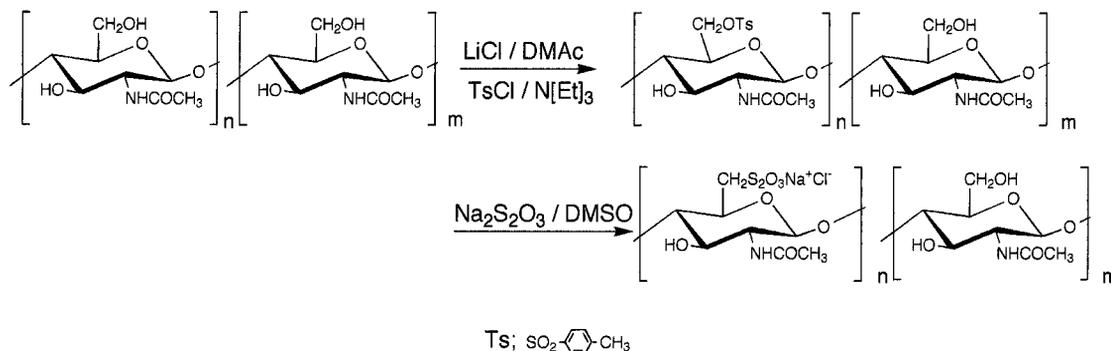
Analysis of Derivatives

Elemental analysis of S₂O₃-chitin was performed at Analytical Center of Tokyo College of Pharmacy. Infrared (IR) spectra were recorded with Perkin-Elmer 1600 Fourier transform (FT) spectro-photometer with a KBr method and film technique.

RESULTS AND DISCUSSION

Synthesis of S₂O₃-Chitin

The preparation of S₂O₃-cellulose via halodeoxy-cellulose was already reported,¹¹ but the chemistry of S₂O₃-chitin has not been reported. We



Scheme 1

could successfully prepare tosyl-chitin in good yield using a LiCl-DMAc solvent system.² Tosyl groups have good potential as leaving groups equal to halogen groups in halodeoxy-cellulose. Then, S_2O_3 -chitin was prepared to react tosyl-chitin with potassium thiosulfate in DMSO solution. (Scheme 1)

The substitution reaction from tosyl groups to S_2O_3 groups proceeded smoothly at 75°C. Under a reaction condition of 75°C for 24 h, the yield of S_2O_3 -chitin obtained was over 90% for tosyl-chitin and 85% for original chitin. The replacement occurred more quickly above 120°C, but the yield decreased drastically because S_2O_3 -chitin did not precipitated thoroughly by precipitant, owing to chitin polymer degradation. It was confirmed by the IR spectra of the filtrate. On the other hand, at temperatures below 50°C, the substitution rarely occurred, and more than a half tosyl groups remained unreacted. This was determined by IR spectra. Similar results were observed on the side reaction of tosylation resulted in Cl-chitin² and other substitution reaction of tosyl-cellulose.^{12,13}

The S_2O_3 -chitin obtained was white or slightly yellow fibrous material. In the IR spectra shown in Figure 1(A)–(C), typical peaks arising from S_2O_3 groups appeared at 632, 1206, and 1231 cm^{-1} , while the peaks of tosyl groups (810, 1370, and 1600 cm^{-1}) almost completely disappeared. This indicates that the replacement was nearly complete. From the result of elemental analysis, it is confirmed that over 80% of tosyl groups was converted into S_2O_3 groups.

As summarized in Table I, S_2O_3 -chitin was soluble in a polar organic solvent, such as DMSO and DMF (1% w/w), and was swelled in methanol and water. The solubility of S_2O_3 -chitin was much higher than that of tosyl-chitin because of its ionic structure and high polarity.

Graft Copolymerization

Photoinduced graft copolymerization using dialkylsulfide is initiated from decomposition of C—S and S—S bonds. Because these dissociation energies are about 72 to 75 Kcal/mol, C—S and S—S bonds are easily decomposed to produce radicals.¹⁴ S_2O_3 -chitin contains similar bonds, and their photolysis are expected to occur easily by irradiation with UV light from a low-pressure mercury lamp.¹⁴ If a monomer susceptible to free

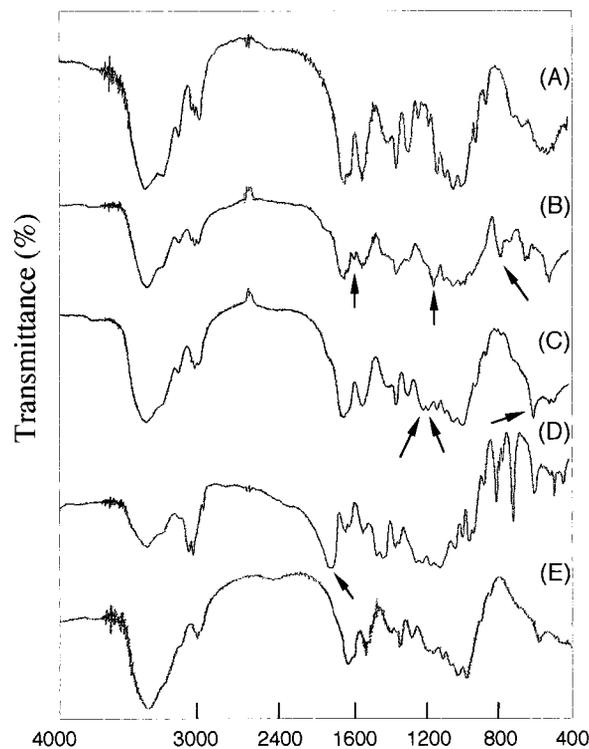


Figure 1 IR spectra: (A) chitin, (B) tosyl-chitin, (C) S_2O_3 -chitin, (D) S_2O_3 -chitin-g-PMMA (quartz tube), and (E) S_2O_3 -chitin-g-PMMA (Pyrex tube).

Table I Solubility of S₂O₃-Chitin

	DMSO ^a	DMAc ^b	DMF ^c	Pyridine	H ₂ O	CH ₃ OH	CH ₃ Cl
Chitin	-	-	-	-	-	-	-
Tosyl-chitin (DS 0.90)	+	+	±	-	-	-	±
S ₂ O ₃ -Chitin (DS 0.49)	±	±	±	±	-	±	±
S ₂ O ₃ -chitin (DS 0.94)	+	±	±	±	±	±	±

+, Soluble; ±, swelled or partially soluble; -, insoluble. Sample concentration: (10 mg/1 g solvent).

^a Dimethylsulfoxide.

^b *N,N*-dimethylacetamide.

^c *N,N*-dimethylformamide.

radical polymerization is present, then graft copolymerization may start as the result of monomer addition onto S₂O₃-chitin (Scheme 2).

Using MMA as the grafting monomer, the degree of grafting to chitin was quite low (22.8%) without catalyst.⁸ Tosyl-chitin, the starting material of S₂O₃-chitin, also showed a low degree of grafting (78.3%) because tosyl groups are easily photodecomposed and change into hydroxyl groups.¹⁵ Eliminated tosyl groups may decompose into various radicals and react with monomers. As the result of their undesirable side reactions, the chain transfer of monomer to trunk polymer was difficult, and homopolymerization dominated in this case. In the absence of chitin, polymerization didn't occur under the same conditions.⁷

Next, MMA was grafted onto S₂O₃-chitin (DS 0.49) in both a Quartz and a Pyrex tube. In a Quartz tube, drastic change and polymerization were observed. In the IR spectra shown in Figure 1(D), typical absorptions attributed to S₂O₃-groups were rarely observed, and new peaks arising from C=O groups of MMA at 1760 cm⁻¹ appeared. It is apparent that the photolysis of S₂O₃ groups occurred.

In the case of a Pyrex tube, grafting did not occur despite the reaction being continued for 6 h. No photolysis was observed in the IR-spectra [Fig. 1(E)]. We believe that since only light above 300 nm in wavelength can be passed through a Pyrex tube, insufficient photochemical energy was supplied to initiate the polymerization reaction. According to the light energy distribution⁹ and the above results, photolysis of S₂O₃ groups requires 253 nm in wavelength.

Monomer Species

To consult the relationship between the monomer species and the polymerization rate, the graft copolymerization of various vinyl monomers to S₂O₃-chitin in aqueous system was performed. As shown in Table II, the total conversion was in the following order: AA > AN > MMA > AAm > St. There are a little relation of monomer E-value to total conversion. Except for AN, the total conversion became higher with monomer polarity. It seems that the propagation of monomer to the trunk polymer was affected with both polarity and monomer affinity to water.¹⁶

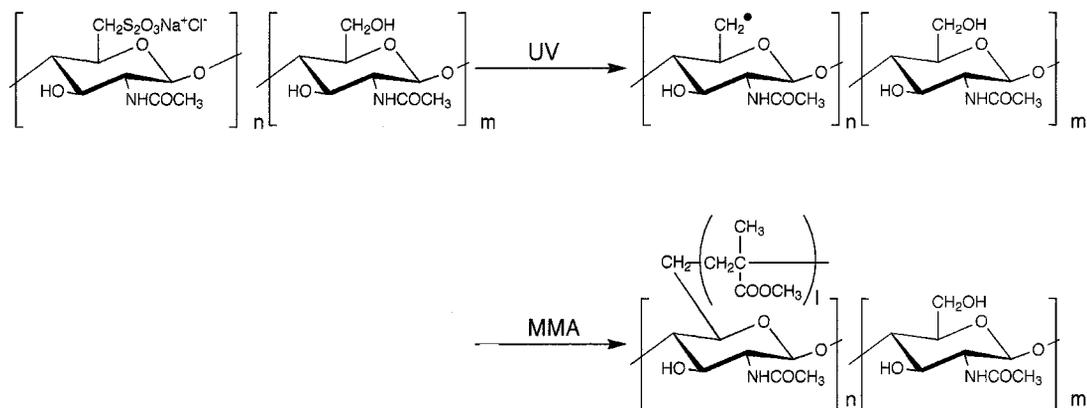
**Scheme 2**

Table II Effect of Monomer Species on Grafting

Monomer	Time (h)	Total Conversion (%)	Degree of Grafting (%)	Grafting Efficiency (%)
AA ^a	1.0	70.79	0.00	0.00
AN ^b	1.0	46.75	278.90	95.67
MMA ^c	1.0	24.40	126.32	42.24
AAM ^d	1.0	17.08	0.00	0.00
St ^e	4.0	3.49	38.51	88.19

S₂O₃-chitin (DS 0.76), 0.15 g; H₂O (12-monomer) mL; [Monomer] 1.57 mol/L; 50°C.

^a Acrylic acid.

^b Acrylonitrile.

^c Methyl methacrylate.

^d Acrylamide.

^e Styrene.

The degrees of grafting with AN and MMA were over 100%, and the grafting efficiencies with AN and St were quite high. In the case of St monomer, the degree of grafting reached only 38% in 4 h. But using AA and AAm, most was homopolymer formation. Because these monomers have high monomer activity, chain transfer to trunk polymer radicals is supposed to be difficult.

In the case of AN, either the degree of grafting and the grafting efficiency were the best, but the extraction procedure was quite difficult because

of its swelled trunk polymer in DMF. Therefore, graft copolymerization with MMA was carried out after here in order to obtain more detailed information.

S₂O₃ Group Content

Graft copolymerization of MMA to different degree of S₂O₃ groups (DS) samples was investigated. As shown in Figure 2, the degree of graft-

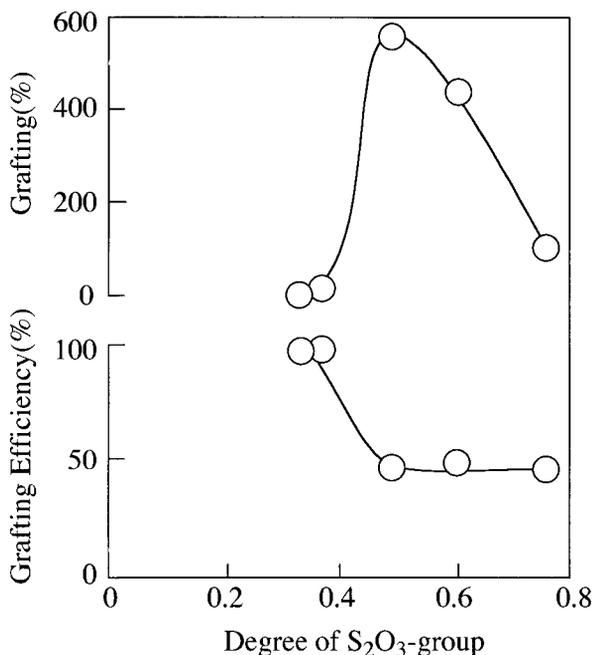


Figure 2 Effect of DS on the degree of grafting and the grafting efficiency: S₂O₃-chitin, 0.15 g; H₂O, 10 mL; MMA, 2 mL (1.57 mol/L); 50°C for 2 h.

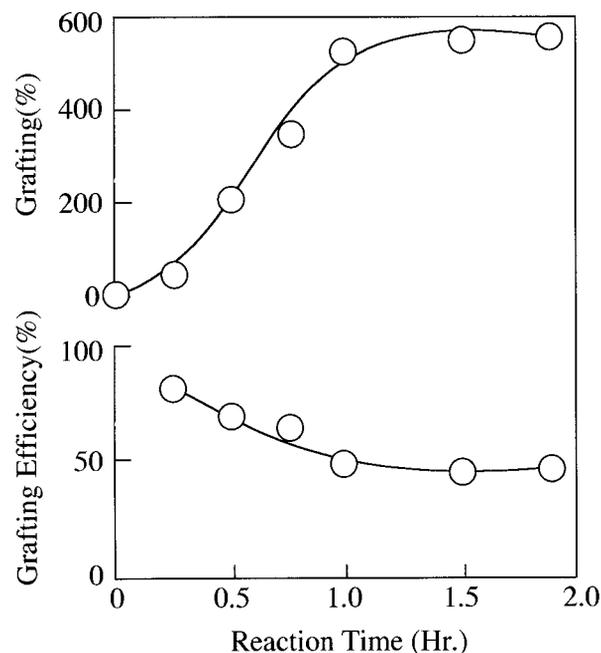


Figure 3 Effect of polymerization time on the degree of grafting and the grafting efficiency: S₂O₃-chitin (DS 0.49), 0.15 g; H₂O, 10 mL; MMA, 2 mL (1.57 mol/L); 50°C.

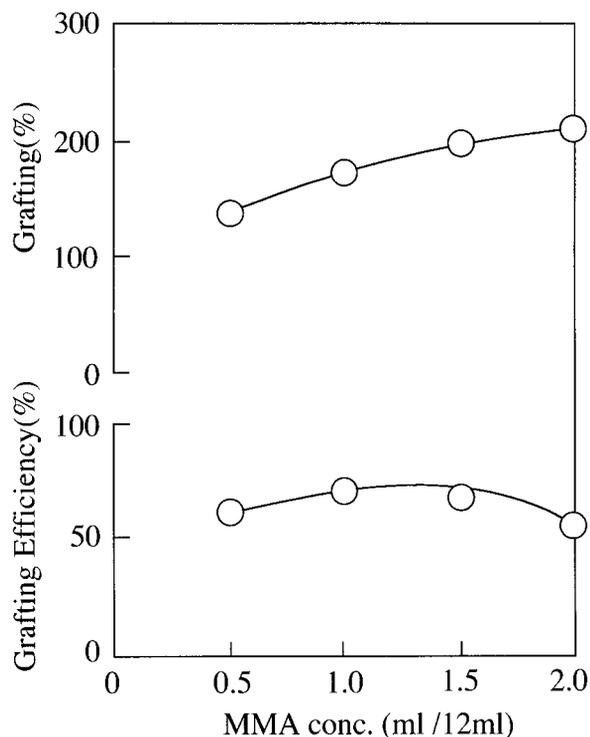


Figure 4 Effect of MMA concentration on the degree of grafting and the grafting efficiency: S_2O_3 -chitin (DS 0.49), 0.15 g; H_2O (12-MMA), mL; $50^\circ C$ for 0.5 h.

ing increased rapidly until DS 0.4 reached the maximum at about DS 0.5, and then decreased rapidly. The grafting efficiency was almost 100% below DS 0.4, but it became smaller with an increase of DS and constant about 50% around DS 0.5. The increase of DS accelerates the graft copolymerization, but more increases also activate the termination reaction. From these results, it is concluded that S_2O_3 groups accelerate the production of chitin radicals and initiate the polymerization; but on the other hand, they participate in the termination reaction with the growing polymer radicals. There exists the optimum DS for this graft copolymerization of S_2O_3 -chitin. Similar results were observed in Oxy-chitin⁷ and *O*-acetyl-chitin.⁸

Polymerization Time

The effect of reaction time on graft copolymerization was studied. As illustrated in Figure 3, the degree of grafting increased rapidly, to a maximum of 530% in 1 h and then became constant. But the grafting efficiency drastically decreased to 50% within 1 h.

Soon after UV irradiation, white emulsion was observed in the polymerization system. Thus, the

rate of polymerization would be quite faster than those of *O*-acetyl-chitin⁸ and Oxy-chitin.⁷ It indicates that the photolysis of S_2O_3 groups is easier than those of *O*-acetyl groups and carbonyl groups.

MMA Concentration

Graft copolymerization with various MMA concentration was carried out at $50^\circ C$ for 30 min. As shown in Figure 4, the degree of grafting increased as monomer concentration increased and reached 200% at 2.0 mol/L. At the same time, the grafting efficiency was around 55–85%.

From these results, it is indicated that the chain transfer of monomer to trunk polymer occurred.

Solvent Concentration

The effect of solvent concentration on grafting was studied in aqueous DMSO and aqueous dioxane systems. DMSO dissolves MMA monomer and, also, S_2O_3 -chitin trunk polymer. But dioxane does not dissolve S_2O_3 -chitin.

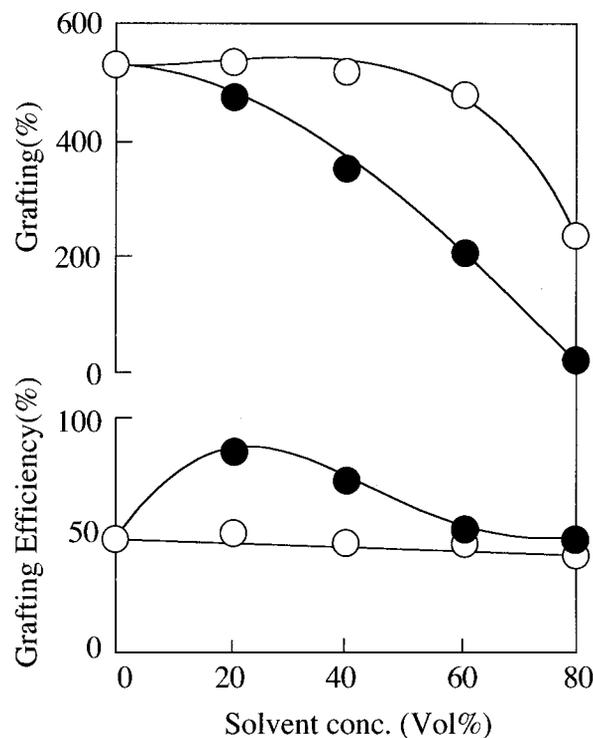


Figure 5 Effect of solvent concentration on the degree of grafting and the grafting efficiency: S_2O_3 -chitin (DS 0.49), 0.15 g; H_2O (10-solvent), mL; MMA, 2 mL (1.57 mol/L); $50^\circ C$ for 1 h. (○) designates DMSO; (●) designates dioxane.

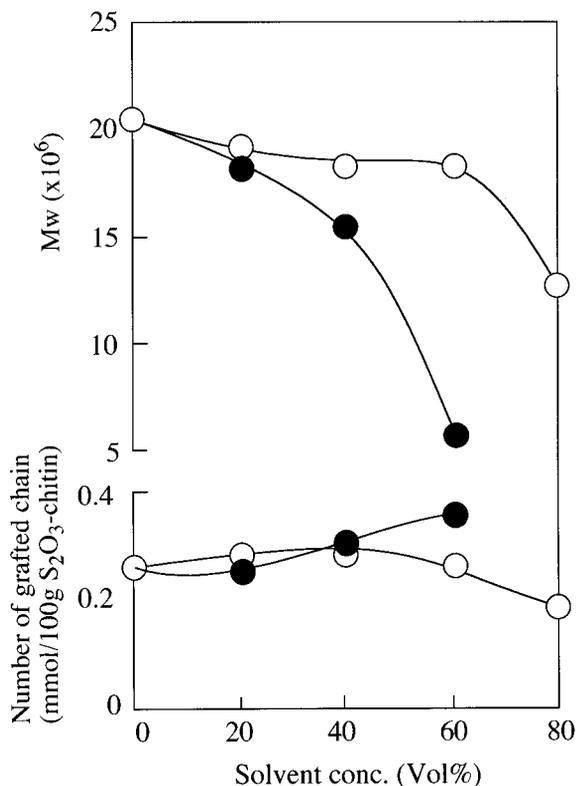


Figure 6 Effect of solvent concentration on molecular weight and apparent number of grafted chain: S_2O_3 -chitin (DS 0.49), 0.15 g; H_2O (10-solvent), mL; MMA, 2 mL (1.57 mol/L); $50^\circ C$ for 1 h. (○) designates DMSO; (●) designates dioxane.

As shown in Figure 5, the degree of grafting decreased with an increase of dioxane concentration and DMSO concentration. The grafting efficiency had no relation with the amount of DMSO concentration and was constant around 50%. The grafting efficiency increased with an increase of dioxane concentration and reached to the maximum at 60%.

The molecular weight of grafted branch showed similar inclination with the degree of grafting shown in Figure 6. It was constant until 60% of DMSO and then became smaller. With an increasing in the dioxane concentration, the degree of polymerization decreased rapidly. The apparent number of grafted chain slightly increased with an increase of solvent concentration but decreased over 60% of DMSO concentration.

From these results, we propose that UV irradiation resulted in the generation of solvent radicals. Increasing solvent radicals caused acceleration of the termination reaction with chitin radicals and with growing polymer radicals.

Therefore, both the grafting efficiency and the degree of grafting decreased. It is considered that optimum solvent concentration also exist. Similar results were observed in the graft copolymerization of *O*-acetyl-chitin described above.

CONCLUSION

S_2O_3 -chitin was prepared by reacting reactive precursor of tosyl-chitin with sodium thiosulfate. In the case of the noncatalytic photoinduced graft copolymerization onto S_2O_3 -chitin, MMA and AN grafted. But St grafted a little, and AA and AAm did not graft at all. The optimum conditions, such as monomer concentration, degree of S_2O_3 groups, and solvent concentration, existed. In spite of the addition of organic solvent, such as DMSO and dioxane, the affinity between monomer and solvent increased and the degree of grafting decreased.

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