Preparation of Chitin/Polystyrene Hybrid Materials by Efficient Graft Copolymerization Based on Mercaptochitin

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ABSTRACT: Graft copolymerization of styrene onto mercaptochitin has been examined. Chitin was first tosylated to give tosylchitin, which was subsequently transformed into mercaptochitin. Athough the graft copolymerization was carried out in suspension, it proceeded efficiently to give chitin derivatives having polystyrene branches, a novel type of hybrid materials composed of a natural polysaccharide and a synthetic polymer. Under appropriate conditions, the grafting percentage reached 970%, indicating the high efficiency of the mercaptochitin as an initiator for the polymerization of styrene. The resulting graft copolymers exhibited glass transition phenomena at 115 °C and showed high swelling in organic solvents as a result of the introduction of polystyrene branches. Hydrolytic degradation of the chitin main chain allowed the isolation of the side chains, and the polystyrene isolated from the graft copolymer with a grafting percentage of 940% had M_n, M_w, and M_w/M_n values of 9.74×10^4, 2.55×10^5, and 2.62. These values indicate that the ratio of the mercapto groups actually used for initiating graft copolymerization was 4%, and a polystyrene chain attached on average to every 45 pyranose units.

Introduction

Chitin is similar to cellulose from the viewpoint of both the structure and abundance in nature but may be a much more useful biomaterial because of the characteristic properties associated with the presence of amino groups. It is considered to have high potential as a specialty polymeric material in various fields such as separation membranes, chelating agents, biodegradable materials, cosmetics and toiletries, and biomedical materials.[1,2] Some specific biological, physiological, and pharmacological activities of chitin are also significant, including antitumor activity, immune-enhancing ability, hypolipidemic activity, hemostatic activity, acceleration of wound healing, promotion of growth of *L. bifidus,* and a virucidal and fungicidal effect. In spite of these interesting properties, chitin has remained an unutilized biomass resource owing to its intractable nature.

Chemical modifications of chitin, though difficult because of insolubility, are thus becoming increasingly important for developing advanced materials based on this amino polysaccharide. Graft copolymerization is one of the promising and desirable modification modes in that it would impart the advantages of synthetic polymers to the polysaccharide. It will afford novel types of tailored hybrid materials composed of the natural polysaccharide and synthetic polymers. Introduction of polymer branches into chitin would enable fine control of the properties, depending on the molecular structure, length, and number of the side chains.

Though graft copolymerization onto chitin has not been studied extensively, some initiation methods for vinyl monomers have been reported: cerium(IV),[3−5] tributylborane,[6] γ-ray,[7] and UV.[8] The reactions, however, have to be conducted under heterogeneous conditions in suspension and are thus generally poor in efficiency and reproducibility. Moreover, the structures of the graft copolymers are complicated and hard to elucidate.

Soluble chitin derivatives have made possible controlled and efficient graft copolymerization and solved the problems arising from the insolubility of chitin. Iodochitin has proved to be an appropriate soluble derivative for efficient graft copolymerization of styrene in solution.[9] Tosylchitin[10] is another soluble derivative for cationic graft copolymerization of 2-methyl-2-oxazoline.[11] The water-soluble chitin,[12] a derivative having acetyl groups randomly at half of the amino groups, is suitable for graft copolymerization of α-amino acid *N*-carboxyanhydrides.[13−15] Although mercaptochitin is not soluble, it is expected to allow efficient graft copolymerization owing to the presence of readily dissociating mercapto groups and considerable swelling in organic solvents. We report here the graft copolymerization of styrene onto mercaptochitin and some properties of the resulting graft copolymers.

Experimental Section

General Procedures. Styrene was purified by distillation. Dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were dried with calcium hydride, distilled in nitrogen under reduced pressure, and stored over 3 Å molecular sieves. IR spectra were recorded with a Jasco IR-700 spectrometer. Thermal properties of the graft copolymers were elucidated with a Seiko SSC-5200 and a DSC unit. GPC was performed with a Jasco 880-PU connected to a Shodex SE-61 RI detector: column, Shodex KD-806M + KD-802; solvent, DMF; standards, polystyrene.

The grafting percentage, defined as follows, was determined with a calibration line used for the graft copolymerization of styrene onto iodochitin in a previous paper.[9] It is based on the absorbance ratios of characteristic bands at 1450 cm^{-1} due to polystyrene and at 1070 cm^{-1} due to chitin in IR spectroscopy.

$$\text{grafting percentage} = [(\text{weight of introduced polystyrene branches})/(\text{weight of chitin main chain})] \times 100$$

Mercaptochitin. Mercaptochitin was prepared from tosylchitin according to a procedure similar to that reported

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Scheme 1

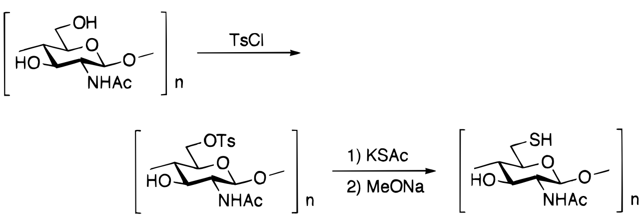

Table 1. Preparation of Mercaptochitins from Tosylchitins

run no.	ds of tosylchitin	ds of mercaptochitin
1	0.52	0.50
2	0.58	0.56
3	0.75	0.70

recently.[16] Tosylchitin dissolved or swollen in DMSO was treated with potassium thioacetate and then *S*-deacetylated with sodium methoxide to give mercaptochitin. The degree of substitution (ds) for the mercapto groups was determined by Ellman's method.[17]

Graft Copolymerization. Pulverized mercaptochitin (ds 0.56; 0.10 g) was dispersed in 6 mL of DMSO, and 2.90 g (60 equiv to pyranose, 110 equiv to mercapto groups) of styrene was added. The mixture was stirred at 80 °C for 48 h in a nitrogen atmosphere and poured into ether. The precipitate was filtered and washed with benzene at room temperature overnight. It was further washed with methanol and dried to give a white powdery material, whose grafting percentage was 970% as determined with the calibration line.[9] The yield of the graft copolymer was 0.41 g (38% recovery). IR (KBr): ν 3400 (O−H and N−H), 3028 and 2924 (C−H), 1660 (C=O), 1601, 1493, and 1450 (phenyl), 1100−1000 (pyranose), 752 and 700 cm^{-1} (phenyl).

The combined filtrates and washings were concentrated under reduced pressure and poured into methanol. The precipitate was washed with methanol several times to give 0.92 g of homopolystyrene as a white precipitate.

Isolation of the Side Chains. To 0.50 g of the graft copolymer with a grafting percentage of 940% was added 300 mL of 12 mol/L hydrochloric acid, and the mixture was heated at 100 °C for 24 h with stirring. The resulting brown solution was evaporated under reduced pressure to give a brown powder, which was extracted with chloroform. The extract was concentrated under reduced pressure and poured into methanol to give 0.24 g (53% recovery) of polystyrene having a terminal glucosamine unit as a light brown powdery material.

Results and Discussion

Mercaptochitin is characterized by considerable swelling ability in ordinary organic solvents and the presence of S−H bonds that undergo homolysis easily on heating to produce free radicals. It is thus expected to efficiently initiate polymerization of vinyl monomers under mild conditions without irradiation or additional initiators. As a typical vinyl monomer, styrene was chosen to examine the graft copolymerization behavior.

Mercaptochitin. Tosylchitin is prepared by the interfacial method between an alkali chitin solution and a chloroform solution of tosyl chloride. It is soluble in polar organic solvents and readily converted into mercaptochitin by the reaction with potassium thioacetate followed by *S*-deacetylation (Scheme 1). The transformation of tosylchitin into mercaptochitin appeared to be quantitative, judging from the IR spectra and ds values of the products as listed in Table 1.

Scheme 2

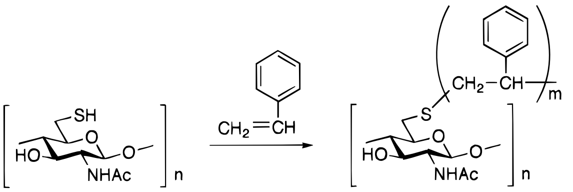

Table 2. Graft Copolymerization of Styrene onto Mercaptochitin[a]

mercaptochitin,[b] g	styrene/ pyranose[c]	solvent, mL	yield, g	grafting,[d] %
0.10	10	6	0.03	40
0.10	30	6	0.14	240
0.10	60	6	0.41	970
0.53	100	30	3.23	940
0.10	150	6	0.43	910

[a] In DMSO at 80 °C for 48 h. [b] ds 0.56. [c] Molar ratio. [d] Determined with the calibration line.[9]

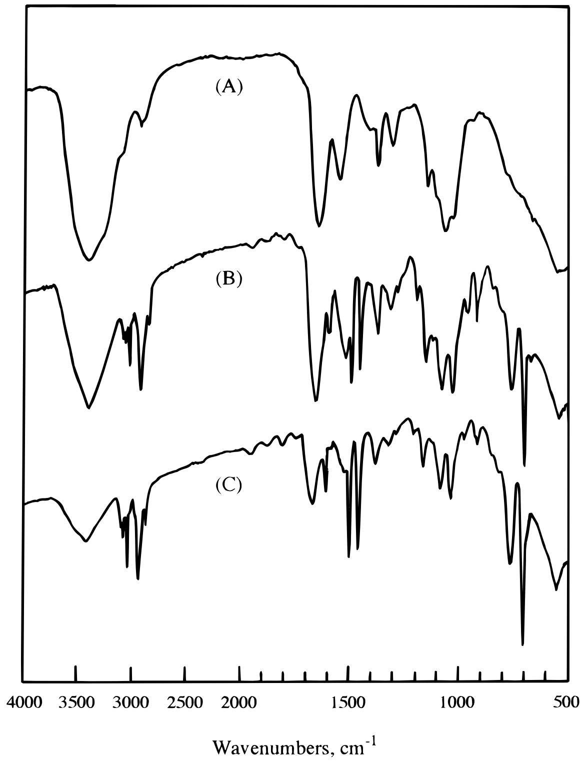

Figure 1. IR spectra of (A) mercaptochitin with a ds of 0.56, (B) chitin-*graft*-polystyrene with a grafting of 240%, and (C) chitin-*graft*-polystyrene with a grafting of 970% (KBr method).

Graft Copolymerization. Mercaptochitin swollen in DMSO was treated with styrene at 80 °C to initiate graft copolymerization at the mercapto groups by a radical mechanism (Scheme 2). Although the reaction proceeded under heterogeneous conditions, the mixture became a white cloudy dispersion after 24 h. The resulting graft copolymer was isolated after 48 h by pouring the mixture into ether and subsequently washing the precipitate thoroughly with benzene to remove polystyrene homopolymer. The chitin-*graft*-polystyrene was obtained as a white powdery material.

The extent of grafting was evaluated in terms of grafting percentage, which is the ratio of the amount of the introduced side chains to that of the main chain. As summarized in Table 2, the graft copolymerization proceeded quite efficiently under these conditions, giving rise to the incorporation of considerable amounts of polystyrene branches. The grafting percentage increased with the amount of styrene monomer added and reached a maximum of 970% with 60 equiv of styrene.

Characterization of the Graft Copolymers. Figure 1 shows the IR spectra of the mercaptochitin and

Table 3. T_g Values of the Graft Copolymers

grafting, %	T_g,[a] °C
240	114.5
940	115.4
970	114.6

[a] Determined by DSC at a heating rate of 20 °C/min.

Table 4. Solubility of the Graft Copolymers[a]

grafting, %	DMSO	DMF	$CHCl_3$	MeOH	H_2O
250	±	±	±	±	−
940	±±	±	±	±	−

[a] ±±, partially soluble or highly swelled; ±, swelled; −, insoluble.

Scheme 3

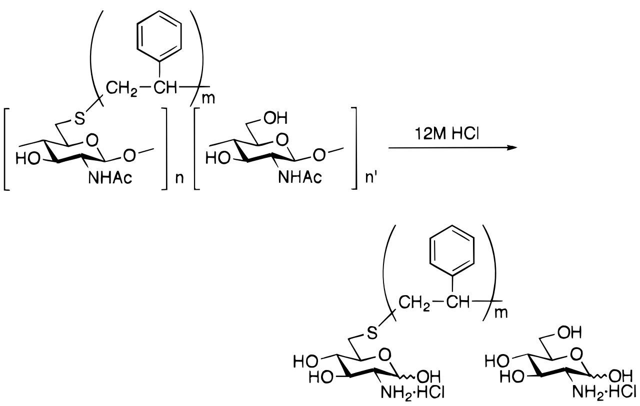

Table 5. Characterization of the Introduced Polystyrene Branches

grafting of copolymer, %	isolated polystyrene				initiation efficiency,[b] %
	yield, %	GPC[a]			
		M_n	M_w	M_w/M_n	
940	53	9.74×10^4	2.55×10^5	2.62	4

[a] In DMF with polystyrene standards. [b] Percentage of the mercapto groups actually used for initiating graft copolymerization.

graft copolymers. On introduction of polystyrene branches into chitin, characteristic bands due to the polystyrene moiety such as those at 3028, 1601, 1493, 1450, 752, and 700 cm^{-1} became increasingly evident as the grafting percentage increased. When the grafting percentage was above 900%, the spectrum was quite similar to that of polystyrene.

Thermal properties, in particular the glass transition, of the graft copolymers are interesting in view of the structure−property relationship and also of practical application. Chitin itself does not exhibit any glass transition temperature (T_g) because of the rigid backbone, but it was recently found that the introduction of long-chain substituents successfully brings about glass transition phenomena.[5,18] The graft copolymers prepared here were also expected to show T_g owing to the incorporated polystyrene branches, and in fact, the differential scanning calorimetry (DSC) analysis indicated the presence of T_g at around 115 °C independent of the grafting percentage as summarized in Table 3.

Although the original chitin shows no appreciable affinity for ordinary solvents, mercaptochitin swells in both water and organic solvents to some extent. The graft copolymers showed even better affinity for organic solvents, but not for water as a result of the introduction of hydrophobic polystyrene branches. They were partially soluble or highly swelled in DMSO but not completely soluble even when the grafting percentage was above 900% as listed in Table 4. They also swelled considerably in low-boiling common solvents.

Characterization of the Side Chains. The graft copolymerization behavior is then discussed in terms of the length and number of the side chains introduced. It is hence necessary to elucidate the molecular characteristics of the polystyrene branches including molecular weight and molecular weight distribution. The molecular weight data will also give important information on the initiation efficiency of the mercapto groups.

The chitin backbone of the graft copolymer was thus hydrolyzed with hydrochloric acid (Scheme 3) to liberate the side chains. The IR spectrum of the hydrolysis product obtained from a graft copolymer with a grafting percentage of 940% was almost identical with that of standard polystyrene, supporting the isolation of polystyrene branches. The isolated polystyrene was then subjected to GPC analysis, and the number-average molecular weight (M_n) and weight-average molecular weight (M_w) were 9.74×10^4 and 2.55×10^5. The polydispersity (M_w/M_n) was thereby 2.62 as shown in Table 5. These values indicate that fairly long polystyrene chains were introduced under these conditions. Based on the grafting percentage and M_n values, the ratio of the mercapto groups actually utilized for initiating the graft copolymerization was calculated to be 4% as included in Table 5, and a polystyrene chain turned out to attach on average to every 45 pyranose units.

Conclusions

Mercaptochitin has proved to be quite suitable for initiating graft copolymerization of styrene under mild conditions. Although the polymerization proceeded in suspension, it was quite efficient to introduce long polystyrene branches. Compared to the conventional methods for the graft copolymerization of vinyl monomers onto chitin, which are marked by the low efficiency, poor reproducibility, and ambiguous molecular structure of the products, the present method appears to be superior particularly in that it is efficient and gives graft copolymers with well-defined structures. The resulting polysaccharide/polystyrene hybrid materials are characterized by the presence of T_g and a high affinity for organic solvents and may thus open a way to new applications of this potentially important biomaterial.

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