Cationic and Radical Graft Copolymerization of Styrene onto Iodochitin

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ABSTRACT: Iodochitin was evaluated as a precursor for graft copolymerization of styrene both by a cationic and a free-radical mechanism. In the presence of Lewis acids, cationic species were formed at the carbons bearing an iodo group, and graft copolymerization of styrene proceeded efficiently in nitrobenzene or somewhat less efficiently in nitromethane. As a catalyst, $SnCl_4$ was superior to $TiCl_4$. Grafting percentages were as high as 800% under appropriate conditions. The polystyrene branches were isolated by hydrolytic degradation of the chitin main chains and characterized by GPC. On irradiation of the iodochitin by an excimer laser, the C–I bonds of iodochitin were cleaved to free radicals which initiated styrene grafting. The grafting percentages were not high in the radical graft copolymerization, but very little homopolystyrene was formed. The resulting chitin-*graft*-polystyrenes were much more soluble or swollen in organic solvents.

Introduction

Although chitin is an abundant biomass resource whose annual production is close to that of cellulose, the insolubility in common organic solvents has delayed its utilization and basic research. Chemical modification of this rigid aminopolysaccharide should lead to an interesting novel type of polymeric material. Our current interest has focused on various modes of chemical modifications. Graft copolymerization onto chitin is one of the most attractive modifications in many respects. It is expected to make possible a wide variety of transformations, and we reported the graft copolymerization of some vinyl monomers onto chitin with cerium(IV) ion.[1] Whereas graft copolymerization onto cellulose has been studied extensively, that onto chitin or chitosan has been explored only recently,[2-7] and such studies were limited to graft copolymerization by a radical mechanism under heterogenous conditions.

We reported the preparation of iodochitins and showed that they were useful precursors for further chemical modifications.[8] In graft copolymerization, they provide interesting trunk polymers because of the possibilities of forming cationic species in the presence of a Lewis acid at the carbon atoms bearing an iodo group and also radical species on UV irradiation. Moreover, iodochitins are soluble in organic solvents, so that graft copolymerization can proceed in solution or a highly swollen state. This leads to a controlled introduction of side chains in terms of numbers and positions, unlike the cerium-initiated process in water where a small number of long side chains are generally introduced. Cationic graft copolymerization of vinyl monomers onto polysaccharides is important since it extends the kind of applicable monomers, but it has only been attempted in the grafting of oxazoline onto cellulose.[9] Iodochitin was therefore evaluated as a versatile chitin derivative suitable for graft copolymerization by both cationic and radical mechanisms.

Experimental Section

General Procedures. IR spectra were recorded on a JEOL JIR-3510 or Jasco IR-700. UV irradiation used an excimer xenon chloride laser, employing a Lamda Physik EMG 101-MSC (wavelength, 308 nm; pulse cycle, 10 Hz; pulse energy, 100 mJ). GPC was performed with a Jasco 880-PU connected to an RI detector (column, Asahipak GS-510; solvent, dimethylformamide; standards, polystyrene).

Materials. Iodochitin with a degree of substitution of 0.58 was prepared from tosylchitin as described previously[8] and dried over phosphorus pentoxide before use. Styrene was washed with 5% aqueous sodium hydroxide and water, dried over sodium sulfate, and distilled under nitrogen at a reduced pressure. It was stored in nitrogen at 5 °C in the dark. Nitrobenzene was washed consecutively with aqueous sodium hydroxide, water, dilute HCl, and water, dried over sodium sulfate, and distilled under nitrogen at a reduced pressure. Nitromethane was dried over calcium chloride and distilled under nitrogen. Dichloromethane was washed consecutively with concentrated sulfuric acid, water, aqueous sodium hydroxide, and water, dried over calcium chloride, and distilled under nitrogen. Dimethyl sulfoxide (DMSO) was distilled over calcium hydride in nitrogen under a reduced pressure. All these solvents were stored over 3-Å molecular sieves in nitrogen. Tin(IV) chloride and titanium(IV) chloride were purified just prior to use by trap-to-trap distillation in a vacuum line and stored in nitrogen. Benzoquinone was sublimed.

Cationic Graft Copolymerization. Iodochitin was placed in a flask equipped with a three-way stopcock, and the flask was purged with dry nitrogen. The atmosphere was replaced with nitrogen five times. To the flask were added nitrobenzene and $SnCl_4$ with syringes at 10 °C. The mixture was stirred for 1 h to give a light-red mixture where iodochitin was swollen. Styrene was then added with a syringe, and the reddish-brown mixture was stirred for 5 h at 10 °C. The polymerization was terminated with methanol, and the mixture was poured into ether/chloroform to dissolve homopolystyrene. The precipitate was collected by filtration, washed with ether, and dried. This isolation procdure was found to be effective in removing homopolystyrene judging by the constancy of weight and IR spectra. The graft copolymer was then treated with 20 mL of 0.5 mol/L methanolic potassium hydroxide for 3 h at room temperature. The product was filtered, washed repeatedly with methanol until free of alkali, and dried to give the graft copolymer: IR (KBr) ν 3400 (OH), 2920 (CH of phenyl), 1660 (amide I), 1600 (phenyl), 1520 (amide II), 1200–1000 (pyranose), 755 and 700 (phenyl) cm^{-1}.

The grafting percentage was defined by

$$\text{grafting percentage} = \frac{\text{wt of introduced polystyrene branches}}{\text{wt of chitin main chain}} \times 100$$

which was calibrated by IR spectroscopy, using mixtures of chitin and polystyrene and relating the composition of these mixtures to the ratio of the absorbance at 1450 cm^{-1} of polystyrene and at 1072 cm^{-1} of pyranose rings (see Figure 1).

Graft copolymerizations in nitromethane and dichloromethane were carried out in a similar manner. These reactions were rapid as suggested by the solidification of the mixtures in nitromethane

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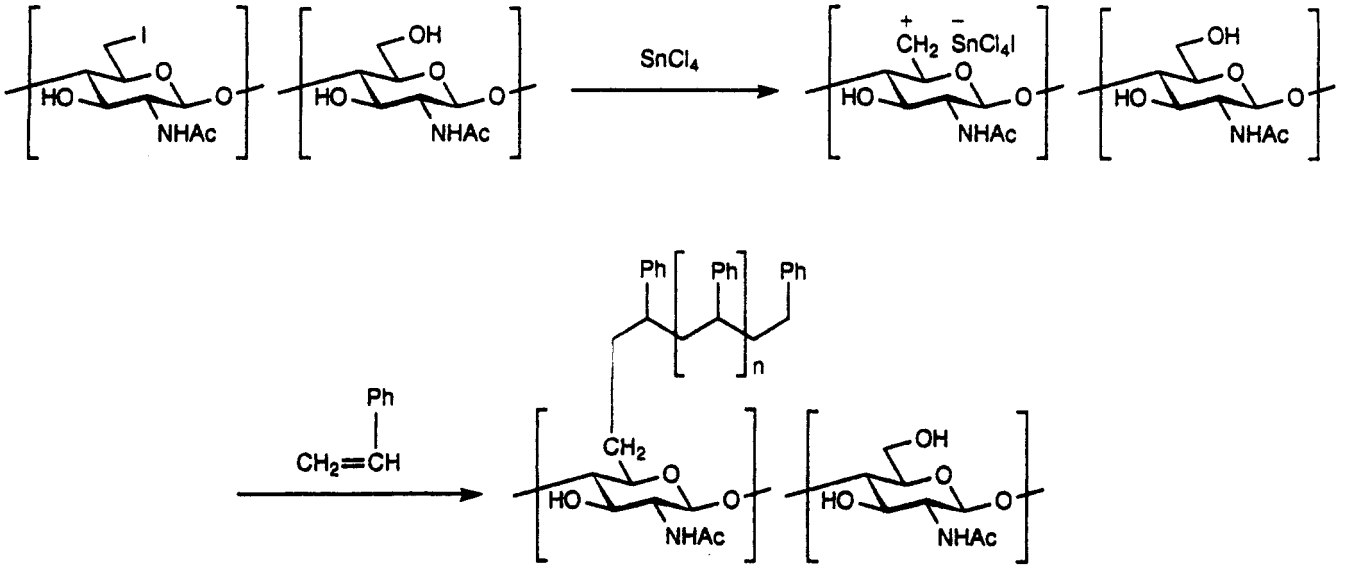
Scheme I



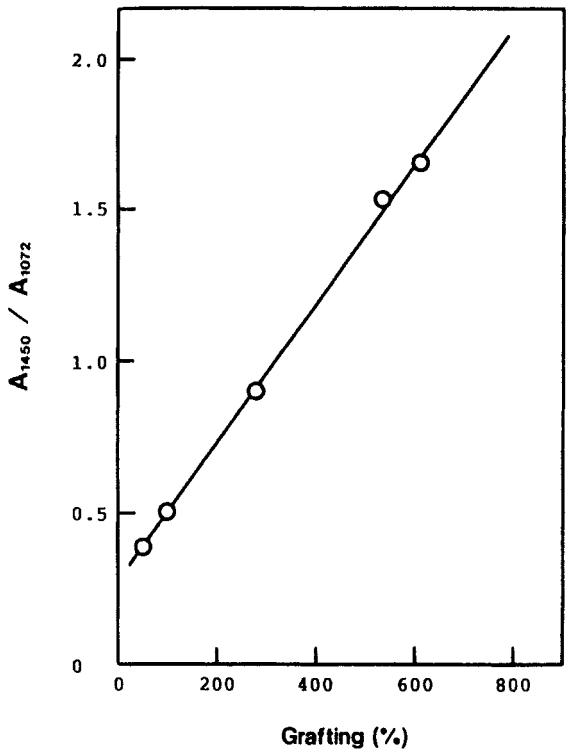


Figure 1. Calibration line to determine the grafting percentage.

and were terminated after 1 h. The products were washed with tetrahydrofuran to ensure removal of homopolystyrene.

Isolation and Characterization of Polystyrene Branches. A dispersion of a graft copolymer in 20 mL of 1 mol/L hydrochloric acid was heated at 100 °C for 7 h. Hydrochloric acid was removed from the resulting solution with a rotary evaporator, and the residue was extracted with warm chloroform. The extract was evaporated, and the residue was dried to give polystyrene whose IR spectrum was virtually identical with that of authentic polystyrene. The number- and weight-average molecular weights, M_n and M_w, were determined by GPC.

Radical Graft Copolymerization. In a quartz flask, 50 mg of iodochitin was dissolved in DMSO, and styrene was added. The solution was frozen in liquid nitrogen and degassed in a vacuum. Thawing and degassing in the frozen state were repeated three times. The finally evacuated flask was irradiated with an excimer laser of 308 nm at a distance of 14 cm from the laser output mirror. After the reaction, the solution was poured into ether. The precipitated product was collected by filtration, washed repeatedly with ether or ether/chloroform, and dried to yield a pale-tan powder. The grafting percentage was determined by the IR calibration line. The IR spectrum was almost identical with that of the copolymer prepared by cationic graft copolymerization.

Results and Discussion

Iodochitins were prepared by tosylation of chitin followed by iodination. For graft copolymerization, an iodochitin with a degree of substitution of 0.58 was used. The iodo groups are most likely attached to the C-6 positions,[8] and side chains are expected to be introduced at these positions. Styrene was chosen as a typical vinyl monomer capable of both cationic and radical polymerization.

Cationic Graft Copolymerization. The copolymerization behavior was examined under various conditions. The formation of cationic species on chitin was first attempted by adding silver triflate or silver tetraborate to the iodochitin in nitrobenzene, but no graft copolymerization took place. Lewis acids such as $SnCl_4$ or $TiCl_4$ were then used, and the effects of solvents such as nitrobenzene, nitromethane, and dichloromethane were examined at 10 °C. Dispersions of the iodochitin in these solvents became light red or pale red on addition of $SnCl_4$ or $TiCl_4$. The iodochitin swelled and was partially soluble in nitrobenzene. It swelled less in nitromethane and did not swell appreciably in dichloromethane. The extent of coloration was thus in this order and heaviest in nitrobenzene. The mixtures became darker on addition of styrene. Reactive cationic species are expected to be formed at the carbons bearing an iodo group, the Lewis acid combining with iodide to give the counterion with graft copolymerization initiated as shown in Scheme I. The products were isolated by pouring into ether/chloroform mixtures which dissolves homopolystyrene formed as a byproduct. The products obtained in nitromethane and dichloromethane contained small amounts of homopolystyrene after washing with this solvent and thus were washed with tetrahydrofuran. After thorough washings, the IR spectra indicated the coordination of some catalyst, and the products were treated with methanolic potassium hydroxide.

The results of small-scale reactions are summarized in Table I. As implied by the coloration of the reaction mixtures, nitrobenzene was the best solvent, and tin chloride was superior to titanium chloride. A small amount of solvent minimized contamination, especially with water, which interferes severely with cationic polymerization. Too

Scheme II

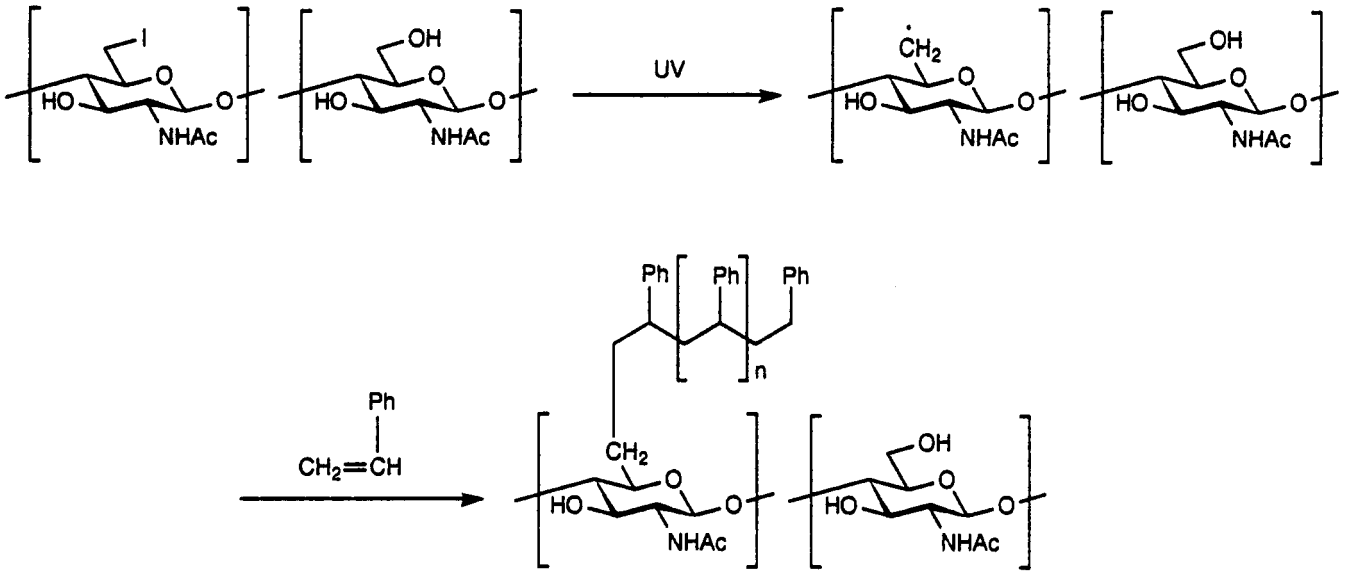


Table I
Cationic Graft Copolymerization under Various Conditions[a]

iodochitin, mg	catalyst (mL)	solvent (mL)	time, h	yield, mg	grafting, %
50	$SnCl_4$ (0.025)	nitrobenzene (2)	5	58	42
49	$SnCl_4$ (0.05)	nitrobenzene (2)	5	60	52
51	$SnCl_4$ (0.10)	nitrobenzene (2)	5	105	300
48	$SnCl_4$ (0.10)	nitrobenzene (4)	5	45	120
50	$SnCl_4$ (0.05)	nitromethane (2)	1	15	60
51	$SnCl_4$ (0.10)	nitromethane (2)	1	34	207
51	$SnCl_4$ (0.10)	nitromethane (4)	1	33	30
51	$SnCl_4$ (0.20)	nitromethane (2)	1	32	108
51	$SnCl_4$ (0.05)	dichloromethane (2)	1	14	49
50	$TiCl_4$ (0.05)	nitromethane (2)	1	35	0
50	$TiCl_4$ (0.10)	nitromethane (2)	1	10	25

[a] Styrene, 1.8 g; temp, 10 °C.

much catalyst decreased the grafting percentage probably because of rapid consumption of the monomer as a result of homopolymerization. The reaction mixtures in nitrobenzene became quite viscous, and those in nitromethane solidified immediately on account of the insolubility of polystyrene in this solvent. The tendency of forming homopolymer depended primarily on the type of catalyst, and with tin chloride the amount of recovered homopolystyrene was always almost quantitative, indicating that most of the styrene monomer fed in large excess for grafting was consumed in the homopolymerization under these conditions. A control reaction in the absence of iodochitin yielded homopolymer quantitatively. In the graft copolymerization with titanium chloride, a much less effective catalyst, the formation of homopolymer was poorly reproducible probably because the activity was readily affected by trace amounts of impurities including water.

The above results favor graft copolymerization with tin chloride in nitrobenzene, and this reaction was studied in more detail on a larger scale for better control of the reaction conditions. As shown in Table II, a grafting percentage as high as 800% was achieved under appropriate conditions. Larger amounts of solvent or catalyst again caused a decrease in grafting percentage. The reaction temperature also influenced the grafting, and at 15 °C the grafting percentage was considerably reduced. At 5 °C, stirring was not efficient due to the closeness to the freezing temperature of the solvent.

The graft copolymers were obtained as white to pale-yellow powdery materials. The IR spectra showed characteristic absorption bands of polystyrene at 2920, 1600, 1450, 755, and 700 cm^{-1} in addition to those of chitin at 3400, 1660, 1520, and 1200–1000 cm^{-1}. A typical spectrum is shown in Figure 2. The graft copolymers were almost soluble in polar solvents such as DMSO, *N*-methyl-2-pyrrolidone, and *N*,*N*-dimethylacetamide containing 5% lithium chloride when the grafting percentage was above 100%, but a small part remained swollen. They swelled even in common low-boiling solvents such as chloroform and tetrahydrofuran.

Table II
Cationic Graft Copolymerization with Tin(IV) Chloride in Nitrobenzene[a]

iodochitin, mg	$SnCl_4$, mL	nitrobenzene, mL	temp, °C	yield, mg	grafting, %
100	0.10	4.0	10	167	600
104	0.20	4.0	10	152	800
101	0.20	8.0	10	64	115
101	0.40	4.0	10	155	470
100	0.20	4.0	5	140	380
100	0.20	4.0	15	145	580

[a] Styrene, 3.6 g; time, 5 h.

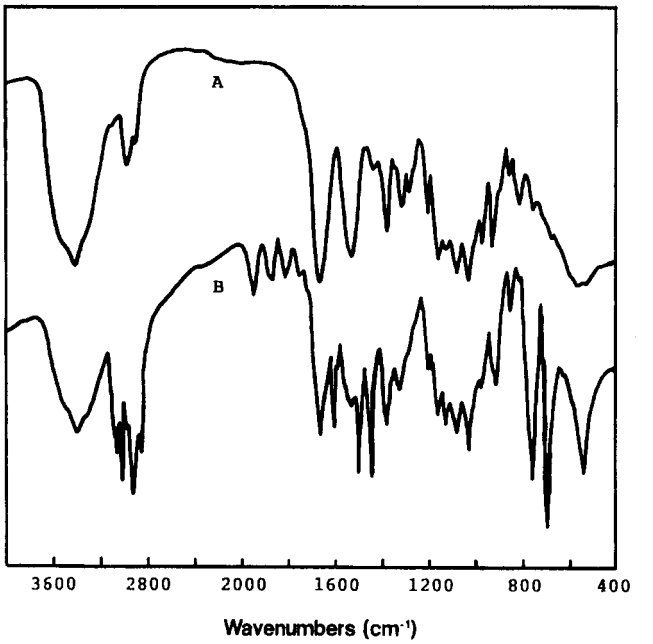


Figure 2. IR spectra of iodochitin with a degree of substitution 0.58 (A) and graft copolymer with 600% grafting (B) (KBr method).

Table III
Acid Hydrolysis of Chitin-*graft*-polystyrene

chitin-*g*-PSt, mg	grafting, %	HCl, mol/L	temp, °C	time, h	yield of PSt		GPC of PSt		
					mg	%	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
101	650	1	100	7	69	79	5.80	8.70	1.50
100	430	6	reflux	5	78	96	3.23	6.46	2.00

Characterization of the Polystyrene Branches. In order to characterize the polystyrene introduced into the chitin, the main chains were degraded to isolate polystyrene side chains. The degradation was first attempted by a sequence of treatments with sodium periodate followed by sodium borohydride and formic acid as reported for graft copolymers of cellulose.[9] Although the product seemed to consist of polystyrene as a major component, the isolation was difficult. Acidic hydrolysis was then applied, and both hydrochloric and sulfuric acids proved suitable for complete hydrolysis of chitin. The products obtained had IR spectra virtually identical with that of polystyrene.

The results are listed in Table III. Number-average molecular weights of the polystyrene branches thus isolated were 5.80×10^4 and 3.23×10^4. The polydispersities, M_w/M_n, were 1.5 and 2.0, indicating that fairly narrow distributions were obtained with the graft copolymerization in a partially dissolved, highly swollen state. These values indicate a polystyrene chain attached on the average to every 44 and 37 *N*-acetylglucosamine units, respectively.

Radical Graft Copolymerization. The iodochitin has labile C–I bonds and was expected to form carbon radical species by photolysis on irradiation with UV light, giving rise to graft copolymers by the free-radical mechanism. No graft copolymers were, however, obtained after irradiation with an ordinary high-pressure mercury lamp.

An excimer laser was anticipated to be sufficiently powerful to cleave the C–I bonds, but no reaction was observed under heterogeneous conditions. Irradiation was thus carried out on a solution of the iodochitin and styrene in DMSO to effect radical graft copolymerization (Scheme II). The products were isolated in ether or ether/chloroform, and the structures were confirmed by IR spectroscopy. The IR spectra were identical with those of the graft copolymers prepared by the cationic process. As shown in Table IV, the grafting percentages were in a range of 50–60%. The grafting was slightly improved by increasing the amount of styrene. The somewhat low grafting percentages may be attributable to the low stability of the nonconjugate radical and also to facile chain transfer to DMSO. Although the grafting percentages were not high, the grafting efficiencies, i.e., the ratios of the weight of grafted polystyrene to the sum of grafted polystyrene and homopolystyrene formed in the reaction, were almost 100%.

Table IV
Radical Graft Copolymerization by UV Irradiation[a]

styrene, g	DMSO, mL	time, h	yield, mg	grafting, %
2.7	0	1	52	0
0.9	2	1	65	52
0.9	2	3	68	49
2.7	2	1	69	63

[a] Iodochitin, 50 mg; temp, room temperature.

Conclusions

Iodochitin proved to be a suitable precursor for graft copolymerization of styrene by both the cationic and radical processes. The cationic graft copolymerization was quite efficient, and high grafting percentages were easily attained under appropriate conditions. Radical graft copolymerization was also possible with excimer laser irradiation. Although the grafting percentages were lower in the radical process, the grafting efficiencies were much higher than those of the cationic process. Graft copolymers based on chitin are of interest because of their solubility, swelling, biodegradability, and compatibility characteristics.

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