Polymer Bulletin 36, 681-686 (1996)

Polymer Bulletin

Chitin/poly(methyl methacrylate) hybrid materials

Efficient graft copolymerization of methyl methacrylate onto mercapto-chitin

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Received: 16 January 1996/Revised version: 19 February 1996/Accepted: 27 February 1996

Summary

Graft copolymerization of methyl methacrylate onto mercapto-chitin has been examined. The copolymerization reaction proceeded efficiently in dimethyl sulfoxide at 80 °C to give chitin-*graft*-poly(methyl methacrylate)s. The grafting percentage increased with the amount of the monomer and reached above 1200% under appropriate conditions. The resulting graft copolymers exhibited remarkable affinity for various common organic solvents.

Introduction

Of various types of polysaccharides, chitin is quite important in view of the significant bioactivities as well as the characteristic physical properties. In particular, it is considered to have much higher possibility than cellulose in regioselective chemical modifications and thereby developing advanced functions. Increasing attention has thus been paid to chitin not only as an abundant unutilized biomass resource, but also as a specialty biopolymer having high potential in various fields including medicine, pharmacology, toiletry, agriculture, food processing, and metal chelation. The actual utilization is, however, quite limited at present owing primarily to the intractable nature. It is being used for water treatment in the form of chitosan salts in only a small quantity.

To explore full potentials of chitin for practical utilization, it is definitely necessary to develop well-controlled modifications, which are generally difficult because of the lack of solubility. Our interest in the preparation of tailored materials based on this amino polysaccharide has prompted us to design new types of efficient modification reactions. For imparting the tractability and characteristics of synthetic polymers, graft copolymerization will have great possibilities. Though the study on the graft copolymerization onto chitin is quite limited, some initiation methods for vinyl monomers have been reported including those with cerium ion (1-3) and UV (4) or γ-ray irradiation (5). However, the efficiency and reproducibility are poor, and moreover, structures of the graft copolymers are not clear, since the reactions have to be conducted under heterogeneous conditions.

Efficient and controlled graft copolymerizations have become possible only recently with some precursors such as iodo-chitin (6), tosyl-chitin (7), and the water-

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soluble chitin (8-10). Mercapto-chitin (11) is also a promising candidate for the polymeric radical initiator owing to the presence of easily dissociating mercapto groups. Moreover, the resulting graft copolymers based on the mercapto-chitin have pro-carboxyl and pro-amino groups, which would be useful for further modifications. Here we report some preliminary results of the graft copolymerization of methyl methacrylate to introduce poly(methyl methacrylate) branches at the mercapto groups of the modified chitin.

Experimental

General

Chitin was transformed into the corresponding 6-deoxy-6-mercapto-chitin (mercapto-chitin) by a series of reactions involving tosylation, thioacetylation, and *S*-deacetylation according to the previously reported procedure (11). It was obtained as a white powdery material, and the one with a degree of substitution (ds) of 0.70 was used in this study. Methyl methacrylate was purified by distillation. Dimethyl sulfoxide (DMSO) was dried with calcium hydride, distilled in nitrogen under reduced pressure, and stored over 3Å molecular sieves. IR spectra were recorded with a Jasco IR-700 spectrometer.

Graft Copolymerization

Mercapto-chitin (ds 0.70, 0.10 g) was added to 6 mL of DMSO, and the mixture was stirred in nitrogen for 3 h at room temperature to allow swelling of the mercapto-chitin. Methyl methacrylate (2.0 g; 50 equiv to pyranose units; 71 equiv to mercapto groups) was added, and the mixture was stirred at 80 °C for 48 h in nitrogen. The resulting white cloudy mixture was poured into methanol, and the precipitate was collected by centrifugation. It was washed with acetone overnight, and the precipitate was separated. The washing procedure was repeated one more time. The solid was further washed with methanol and dried to give 0.23 g of the graft copolymer as a white powdery material. The grafting percentage was 250% as determined with the calibration curve in Figure 1. IR (KBr): ν 3445 (O-H), 1733 (C=O), 1240 (C-O-C), and 1150-1000 cm^{-1} (pyranose).

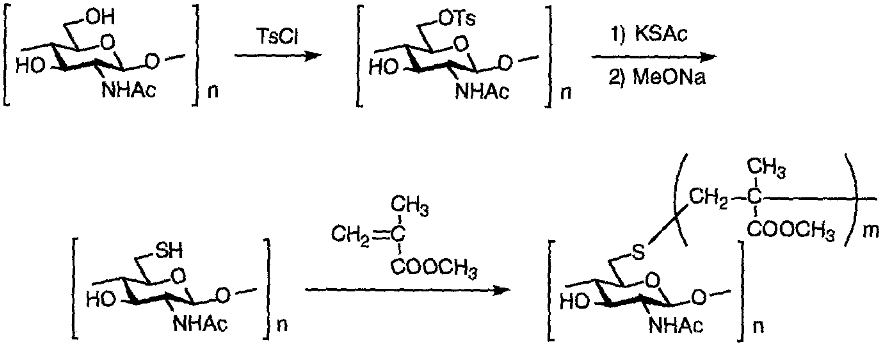
The combined washings were concentrated under reduced pressure and poured into methanol to precipitate poly(methyl methacrylate) homopolymer. After drying, it weighed 0.34 g.

Grafting Extent and Solubility

Extent of grafting was expressed in terms of grafting percentage which was determined with a calibration curve as discussed in the text. Qualitative solubility of the graft copolymers was examined in excess solvents and assessed as follows: ±± for the products swelling highly to give transparent gels with partial dissolution, ± for those with ordinary swelling, and – for those with no appreciable swelling.

Results and discussion

Mercapto-chitin is conveniently prepared from tosyl-chitin (12) by treating with potassium thioacetate in DMSO solution and the subsequent *S*-deacetylation with methoxide (11). As apparent from the fact that thiol compounds are effective chain transfer agents in radical polymerization, the mercapto group dissociates easily to free radicals. In the presence of vinyl monomers, therefore, mercapto-chitin would initiate graft copolymerization by a radical mechanism. Methyl methacrylate was chosen here as an interesting vinyl monomer to diversify the properties of the chitin-derived graft copolymers (Scheme 1).



Scheme 1

Mercapto-chitin is not soluble, but swells in various common organic solvents as well as water. When mercapto-chitin swollen in DMSO was treated with methyl methacrylate at 80 °C in nitrogen, the mixture became cloudy and almost homogeneous in 24 h. The product was isolated in methanol after 48 h reaction and washed thoroughly with acetone to remove the monomer and by-product, poly(methyl methacrylate) homopolymer.

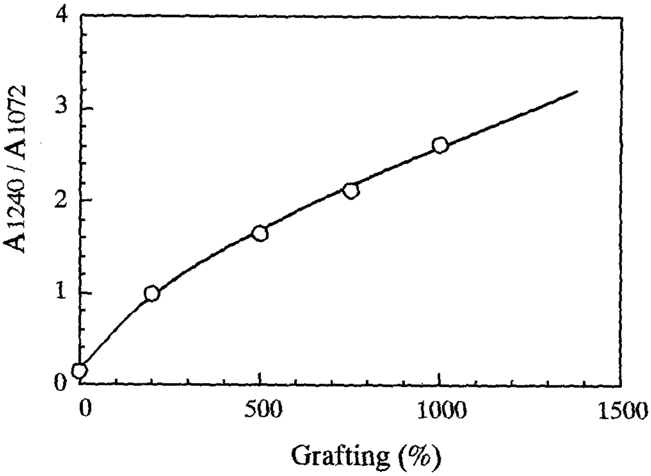


Figure 1. Calibration curve for determining the grafting percentage.

The grafting behavior was examined on the basis of the grafting percentage that is defined as the ratio of the weight of introduced branches to that of the chitin main chain.

$$\text{grafting percentage} = (\text{wt of introduced branches} / \text{wt of chitin main chain}) \times 100$$

The grafting percentages were determined with a calibration curve obtained by IR spectroscopy using mixtures of poly(methyl methacrylate) and chitin. Absorbance ratios of a band at 1240 cm^{-1} characteristic of poly(methyl methacrylate) to that at 1072 cm^{-1} due to chitin were plotted against the mixing ratios, hence the grafting percentages, as illustrated in Figure 1.

As evident in Figure 2, the grafting percentage increased markedly with the amount of the monomer under these conditions. With a monomer amount above 750 equivalents, a grafting percentage of more than 1000% was readily achieved.

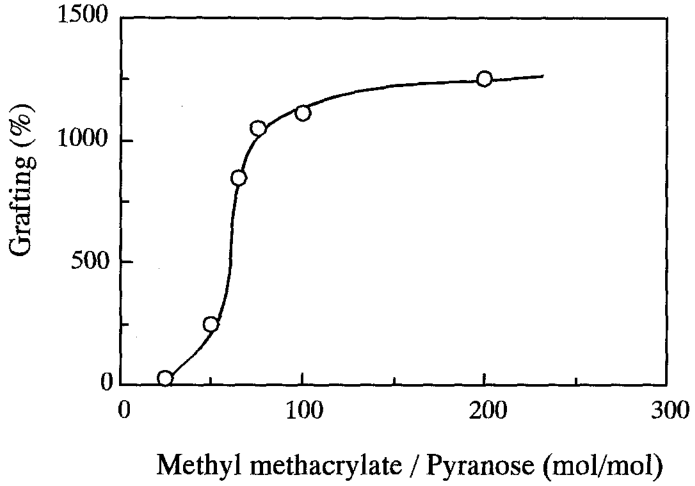


Figure 2. Graft copolymerization of methyl methacrylate onto mercapto-chitin.

As a result of the graft copolymerization, the IR spectra of the products showed characteristic absorption bands including the strong one at 1733 cm^{-1} due to the incorporated poly(methyl methacrylate) branches, and they became more and more evident as the grafting percentage increased. When the grafting percentages were high, the spectra were quite similar to that of poly(methyl methacrylate) itself as shown in Figure 3.

The resulting graft copolymers, chitin-*graft*-poly(methyl methacrylate)s, were obtained as white powdery materials. They exhibited a high affinity for various solvents unlike the original chitin and swelled in most common organic solvents as summarized in Table 1. The graft copolymers with high grafting percentages swelled considerably even in low-boiling solvents such as chloroform and methanol, and were partially soluble with high swelling in DMSO, *N,N*-dimethylformamide, benzene, and dichloromethane.

Although the mercapto-chitin swells in water as well as in organic solvents, the derived graft copolymers showed no apparent swelling in water.

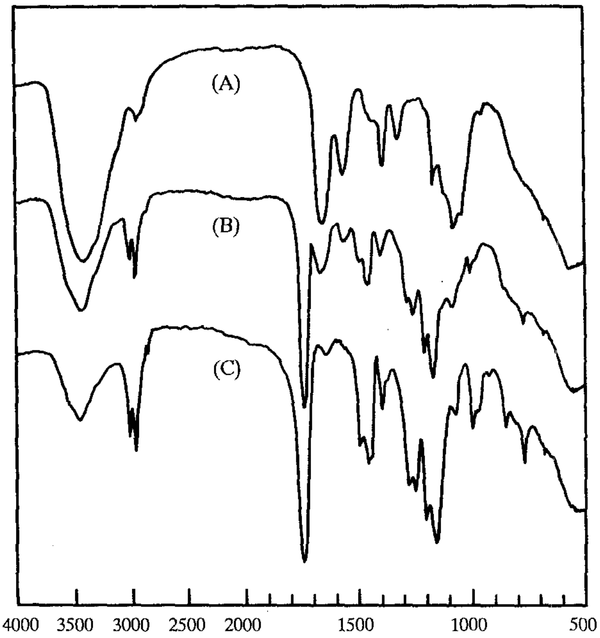


Figure 3. IR spectra of (A) mercapto-chitin, (B) graft copolymer (grafting, 250%), and (C) graft copolymer (grafting, 1250%) (KBr method).

Table 1

Solubility of the Graft Copolymers[a]

Grafting (%)	Solubility					
	DMSO	DMF	Benzene	CH_2Cl_2	MeOH	H_2O
320	±	±	±	±	±	–
1110	±±	±±	±±	±±	±	–

[a] ±±, highly swelled and partially soluble; ±, swelled; –, insoluble.

Consequently, the graft copolymerization of methyl methacrylate onto the mercapto-chitin has thus proved to proceed efficiently with quite high grafting percentages owing to the presence of the active mercapto groups and significant swelling of the mercapto-chitin. The resulting chitin-*graft*-poly(methyl methacrylate)s would be useful as a new type of natural/synthetic hybrid materials exhibiting a marked affinity for organic solvents. Hydrolysis of the graft copolymers will convert the side chain ester groups and the C-2 acetamide groups into carboxyl and free amino groups, which will enable imparting additional hydrophilic and amphoteric characters to the graft copolymers.

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