Heterogeneous Graft Copolymerization of Chitosan Powder with Methyl Acrylate Using Trichloroacetyl−Manganese Carbonyl Co-initiation

David W. Jenkins† and Samuel M. Hudson*

Fiber and Polymer Science Program, Box 8301, North Carolina State University, Raleigh, North Carolina 27695-8301

Received July 27, 2001; Revised Manuscript Received February 15, 2002

ABSTRACT: A highly deacetylated chitosan powder was successfully trichloroacetylated under heterogeneous conditions. The trichloroacetylated chitosan powder was subsequently graft copolymerized heterogeneously with methyl acrylate using a $Mn_2(CO)_{10}$ co-initiator photoactivated with 436 nm light at room temperature. Reaction products were extracted with acetone in an attempt to separate homopolymer from the grafted powder. Portions of the grafted material (presumably surface grafted chitosan) were also removed from the bulk of the grafted powder. After monitoring the weights of reaction product and total polymer extracted from the reaction product (polymeric extract), gel permeation chromatography was used to resolve the polymeric extract into two separate species, assumed to be the grafted chitosan and homopolymer. With this general technique, graft and homopolymer yields for a series of grafting reactions were obtained. Graft yields greater than 600% (based on a percent weight increase of trunk polymer) were obtained, while 20−30% of the poly(methyl acrylate) formed was homopolymer.

Introduction

Chitin and chitosan continue to be underutilized natural polymers. Chitin, a homopolymer comprised mainly of 2-acetamido-2-deoxy-β-D-glucopyranose units, serves as the major structural material, in the form of microfibrils, in various marine invertebrates, insects, fungi, and yeasts.[1] Chitosan, the N-deacetylated derivative of chitin, is obtained by heating chitin in concentrated NaOH. Chitosan is the more tractable of the two materials (being soluble in a aqueous acidic medium), and thus chitosan is more readily processed into different structural materials (films and fibers).[2] The repeat structures of chitin and chitosan are shown in Figure 1.

Interest has developed in combining the properties of chitosan with those of synthetic polymers via free radical graft copolymerization.[3] This is a useful way to modify fiber and film surfaces. The general approach with this method is that free radicals are created along the chitosan backbone, which in the presence of vinyl monomer leads to the formation of grafted chains. Several different initiation methods have been utilized for chitosan grafting, for example, the ceric ion,[4−7] Fenton's reagent,[8−10] exposure to γ-radiation,[11−13] and common free radical initiators[14,15] (azobis(isobutyronitrile) and ammonium persulfate).

Generally, the methods cited above create relatively large amounts of free radicals in solution due to a nonspecific initiation mechanism with the chitosan backbone, which encourages the formation of homopolymer. Homopolymer is an unwanted side product of graft copolymerization; not only does it make characterization of the grafted derivative difficult, but it also wastes monomer. The ceric initiation mechanism, however, is much more specific to the chitosan backbone. Another aspect of the ceric initiation method is that it typically

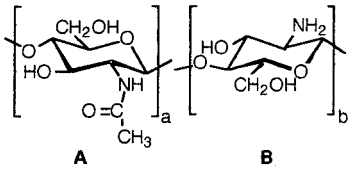


Figure 1. Chemical repeat structures of chitin (A) and chitosan (B).

is conducted under aqueous acidic conditions to promote higher rates of initiation.[16] The acidic ceric initiation method thus prevents the graft copolymerization of chitosan fibers and films, due to chitosan's solubility in this medium. Alternative initiation methods should be attempted that offer specific macroradical formation, while not requiring aqueous acidic conditions and to have the potential to graft copolymerize chitosan films and fibers.

Bamford describes a variety of radical initiating systems that involve organohalide/metal carbonyl co-initiators.[17,18] For example, manganese carbonyl can be photoactivated as shown in eqs 1 and 2 to react with trichlorinated carbons to generate carbon-based radicals[19−21] capable of initiating vinyl polymerizations.

$$Mn_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} 2Mn(CO)_5^{\bullet} \quad (1)$$

$$R{-}CCl_3 + {}^{\bullet}Mn(CO)_5 \rightarrow R{-}{}^{\bullet}CCl_2 + ClMn(CO)_5 \quad (2)$$

The exact structure of the activated manganese species appears to be dependent on the wavelength range utilized for excitation.[21]

Trichloroacetyl/$Mn_2(CO)_{10}$ photoinitiation at room temperature allows specific macroradical formation without requiring acidic conditions.[22−25] The purpose of this work is to investigate the graft copolymerization of chitosan powder with methyl acrylate using $Mn_2(CO)_{10}$/trichloroacetyl photoinitiation (436 nm) at 25 °C. Methyl acrylate has been successfully polymerized with this photoinitiating system.[25] The strategy for the synthesis

† Current address: School of Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA 30332.
* To whom correspondence should be addressed.

10.1021/ma011336b CCC: $22.00
Published on Web 03/26/2002

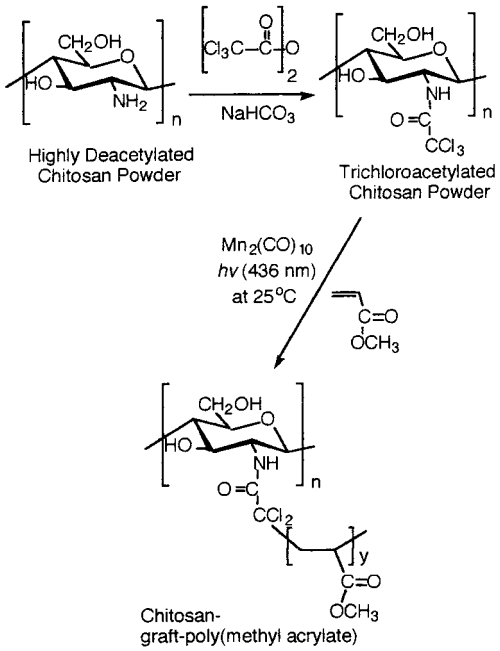


Figure 2. Synthetic scheme for graft copolymerization of chitosan with methyl acrylate using a trichloroacetyl-$Mn_2(CO)_{10}$ co-initiator system. O-Trichloroacetylation of chitosan is not shown in the scheme for simplicity.

is outlined in Figure 2. Highly deacetylated chitosan powder will be heterogeneously trichloroacetylated followed by the photoinitiated grafting with methyl acrylate under a variety of conditions such as different concentrations of monomer and $Mn_2(CO)_{10}$. The respective graft and homopolymer yields will be determined.

Experimental Section

Materials. Chitosan flake (1 part), 80−85% deacetylated from Pronova Biopolymer, Inc., was combined with 10 parts of a 20% (w/w) NaOH solution and kept at 5 °C for at least 24 h. The mixture was filtered, washed with distilled water until neutral to pH paper, and allowed to air-dry. The chitosan (1 part) was further deacetylated by adding to 20 parts of 50% (w/w) NaOH and mixed at 120 °C for 2 h under N_2. The chitosan was filtered, washed with distilled water until neutral to pH paper, and allowed to air-dry. This procedure was performed twice on the chitosan in order to obtain a high degree of deacetylation. The degree of deacetylation for the chitosan was approximately 96.6 ± 0.3% according to potentiometric titration.[26,27] The viscosity-average molecular weight of the chitosan[27,28] was 5.5×10^5 g/mol. The deacetylated flake was ground to pass through a 60 mesh screen and dried at 60 °C for 10 h under vacuum. Elemental analysis: Found: C, 43.8; H, 6.92; N, 8.36; Cl, 0.0.

Sodium bicarbonate, ethyl ether, and acetone were used as received from Fisher. Methylene chloride (stabilized with amylene) was obtained from Fisher and stored over molecular sieves. Trichloroacetic anhydride (95%) was used as received from Aldrich. Ethyl acetate used in grafting reactions was HPLC grade from Fisher and was stored over molecular sieves. Methyl acrylate (Aldrich, 99%) (300 mL) was washed four times with 100 mL of a 5% (w/w) NaOH, 20% (w/w) NaCl solution, and four times with 100 mL of distilled water. The washed methyl acrylate was dried with 20 g of $CaCl_2$ for 30 min, then dried overnight with molecular sieves, and distilled from CaH_2 before polymerizations. Manganese carbonyl ($Mn_2(CO)_{10}$) (Aldrich, 98%) was sublimed[29] under vacuum at 50 °C and stored under Ar in a refrigerator until needed.

Methods. All infrared spectra were obtained from samples in KBr pellets using a Nicolet 510P FT-IR spectrophotometer. All solid-state CP-MAS ^{13}C NMR spectra were obtained at 50 MHz on a Chemagnetics CMC 200S NMR spectrometer with high-power ^1H dipolar decoupling at 50 kHz. The spinning speed was 4 kHz with a spectral width of 30 kHz in 2K data points zero-filled to 8K before the Fourier transform. The contact time was 2.00 ms, and a 3 s pulse delay was used. Gel permeation chromatography relative to PMMA standards was conducted at 25 °C using three Styragel columns (guard column, 10^4 Å, 10^2 Å), THF as eluant at 1.0 mL/min, and a Waters differential refractometer R401.

Trichloroacetylation of Highly Deacetylated Chitosan Powder. A mixture of highly deacetylated chitosan powder (60 mesh) (4.0 g, 0.024 mol of NH_2 groups), sodium bicarbonate (40.3 g, 0.48 mol), and trichloroacetic anhydride (220 mL, 1.2 mol) in methylene chloride (500 mL) was refluxed for 24 h. The product was then filtered and shaken with a 1.4 M sodium bicarbonate (aqueous) solution (2.0 L) for approximately 10−20 min (until effervescence was no longer observed). The product was filtered, washed with distilled water until neutral to pH paper, and dried. IR (cm^{-1}): 1770 (O-trichloroacetyl C═O), 1700 (N-trichloroacetyl C═O), 1530 (N−H of N-trichloroacetyl), 845, 820, 760, 670 (CCl_3). Solid-state CP-MAS ^{13}C NMR: 57.28 (C-2), 60.36 (C-6), 74.49 (C-3,5), 83.2 (C-4), 92.06 (CCl_3), 105.39 (C-1), 163.96 (trichloroacetyl C═O). Elemental analysis: Found: C, 40.38; H, 6.27; N, 7.29; Cl, 7.70. Using the N and Cl content to calculate the total moles of repeat groups (RG) and trichloroacetyl groups (TCAG), respectively, per weight of sample, the mole ratio of TCAG/RG was found to be 0.14 (on a per weight basis there are 0.0723 mol of trichloroacetyl per 100 g of trichloroacetylated chitosan powder). To calculate the individual extents of N- and O-trichloroacetylation, elemental analysis was obtained from a 50 mg sample of trichloroacetylated chitosan that was placed in 10 mL of 0.01 M $NaOCH_3$ in methanol at room temperature for 48 h (in order to cleave ester linkages), filtered, washed with methanol, washed with distilled water until neutral to pH paper, and dried (found: C, 41.11; H, 6.3; N, 7.3; Cl, 4.76). Based on these sets of data, the degrees of N- and O-trichloroacetylation were calculated to be 0.09 and 0.025, respectively.

Graft Copolymerization of Trichloroacetylated Chitosan Powder. An example procedure for synthesizing grafted chitosan is provided below. A cellulose extraction thimble was extracted with ethyl ether, placed in a weighing bottle, dried at 70 °C under vacuum for 3 h, and weighed (W_1). Trichloroacetylated (TCA) chitosan powder (~40 mg, 2.9×10^{-5} mol of TCA groups) was placed in the thimble, dried at 70 °C under vacuum for 3 h, and weighed (W_2). The dried TCA chitosan, $Mn_2(CO)_{10}$ (11.2 mg, 2.9×10^{-5} mol), methyl acrylate (1.1 mL, 0.012 mol), and ethyl acetate (2.9 mL) were added to a 10 mL test tube equipped with a magnetic stir bar. With continual stirring, the contents were purged with Ar for 30 min at 25 °C in the dark. With continual purging and stirring, the light source was turned on and the polymerization was conducted for 30 min; the light (436 nm at 150 W) was piped into the tube using an Oriel instruments light source (500 W mercury arc lamp: model 68810) equipped with a 436 nm interference band-pass filter and dichroic mirror. To quench the reaction, the light source was turned off and 1 mL of 0.1 M hydroquinone (Fisher, 99%) in ethyl acetate was added, followed by ~2 min of stirring. The reaction solution was filtered through the thimble. The filtrate was added to excess (50/50) hexane/ethyl ether to precipitate any homopolymer that had passed through the thimble and was subsequently filtered through the thimble. The thimble contents were extracted with ethyl ether, dried at 70 °C under vacuum for 3 h, weighed (W_3), extracted with acetone for 24 h (in an attempt to remove homopolymer), dried at 70 °C under vacuum for 3 h, and weighed (W_4). The polymer which was collected in the acetone extract (after drying) was sent for N elemental analysis and subsequently was analyzed with GPC. The GP chromatograms were observed to have two main peaks; the area under the high molecular weight peak divided by the area under the entire chromatogram was taken as the fraction of graft copolymer in the polymer extract, α. Graft and homopolymer yields were calculated as shown in eqs 3 and 4, respectively. Grafting yield is based on a percent weight increase relative

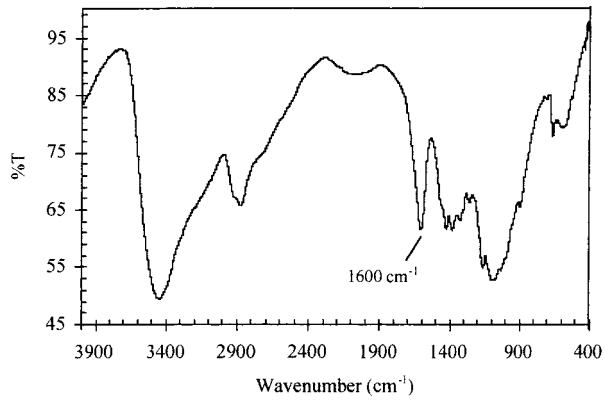


Figure 3. FTIR spectrum of highly deacetylated chitosan powder.

to the trunk polymer weight, while homopolymer yield is based on the weight of total polymer formed.

$$\% \text{ G} = 100 \times \frac{(\text{wt of graft copolymer}) - (\text{wt of trunk polymer})}{(\text{wt of trunk polymer})}$$

$$= 100 \times \frac{(W_4 - W_1 + \alpha(W_3 - W_4)) - (W_2 - W_1)}{W_2 - W_1} \quad (3)$$

$$\% \text{ H} = 100 \times \frac{\text{wt of homopolymer}}{\text{wt of total polymer formed}} = 100 \times \frac{(1 - \alpha)(W_3 - W_4)}{W_3 - W_2} \quad (4)$$

Using the observed weights and α (W_1, 23.1293 g; W_2, 23.1690 g; W_3, 23.1992 g; W_4, 23.1869 g; α, 0.10) for this experiment, graft and homopolymer yields were calculated to be 48% and 37%, respectively (IR of grafted chitosan powder; 1735 cm^{-1}, C═O of poly(methyl acrylate) grafted chains). Total monomer conversion was only 2.9%.

Results and Discussion

Synthesis of Trichloroacetylated Chitosan Powder. The first step toward grafting the chitosan is to synthesize a trichloroacetylated chitosan (from highly deacetylated chitosan powder) to serve as a co-initiator for the manganese carbonyl photoinitiation method. The FTIR and solid-state CP-MAS ^{13}C NMR spectra of the highly deacetylated chitosan powder are shown in Figures 3 and 4, respectively. Figure 5 provides typical solid-state ^{13}C NMR chemical shift data for chitin and chitosan. Figures 3 and 4 show no evidence of *N*-acetyl groups in the chitosan powder due to the absence of the characteristic IR bands (C═O, 1645 cm^{-1}; N−H, 1550 cm^{-1}; the IR band at 1600 cm^{-1} is due to the NH_2 deformation of the primary amine) and ^{13}C chemical shifts for the acetyl amide moiety.

Figure 6 provides the FTIR spectrum of the trichloroacetylated chitosan synthesized from highly deacetylated chitosan. Evidence of trichloroacetylation is shown by absorptions at approximately 1770, 1700, 1530, 845, 820, 760, and 670 cm^{-1}. The absorption at 1770 cm^{-1} is assigned to the carbonyl stretch of the O-trichloroacetyl based on the IR spectrum of ethyl trichloroacetate.[32] Absorptions at 1700 and 1530 cm^{-1} are assigned to the carbonyl stretch and the N−H deformation of the N-trichloroacetyl, respectively.[33] Since C−Cl bonds generally absorb in the range of 900−600 cm^{-1} and because both ethyl trichloroacetate and 2,2,2-trichloroacetamide have similar absorptions in this region,[32] the peaks at 845, 820, 760, and 670 cm^{-1} are assigned to the CCl_3 moiety.

Figure 7 shows the solid-state CP-MAS ^{13}C NMR spectrum of the trichloroacetylated chitosan. There are two new chemical shifts at approximately 164 and 92 ppm, which are assigned to the carbonyl carbon and trichloromethyl carbon of the trichloroacetyl group, respectively. These peak assignments compare well with model compounds such as, 2,2,2-trichloroacetamide and ethyl trichloroacetate which have carbonyl chemical shifts at 163.1 and 161.9 ppm, respectively, accompanied by trichloromethyl carbon chemical shifts of 93.0 and 89.9 ppm, respectively.[34] Degrees of substitution for N- and O-trichloroacetylation were calculated to be approximately 0.09 and 0.025 according to N and Cl elemental analysis. The trichloroacetylation yields for this powder are relatively low, considering the high ratio of trichloroacetic anhydride to chitosan amine employed (50/1). However, extremely high ratios are not uncommon for chitosan acylations. For example, ratios of acylating reagent to chitosan amine were in the range of 20−300 in order to obtain reasonable degrees of acylation on a highly swollen chitosan.[35]

Graft Copolymerization of Trichloroacetylated Chitosan with Methyl Acrylate under Photoinitiating Conditions Using $Mn_2(CO)_{10}$. We envision the grafting reaction as a surface modification. Since the highly deacetylated chitosan powder was trichloroacetylated in methylene chloride as a slurry (heterogeneously), the trichloroacetyl groups should predominantly reside on the outer core of the chitosan powder particles. Upon exposure to the light, the activated manganese species would be generated in solution and subsequently react with the trichloroacetyl moieties on the outer surface of the trunk polymer powder, promoting specific macroradical formation; the trichloroacetylated chitosan powder is not soluble in the polymerization medium. Once the macroradicals react with the methyl acrylate present in solution, grafted chains will begin to grow from the particle's surface. Since the nature of initiation is mechanistically highly specific, homopolymer should only result from the chain transfer of growing grafted chains to either the monomer or the solvent.

As outlined in Table 1, a series of grafting experiments were conducted with the trichloroacetylated chitosan, at varying concentrations of methyl acrylate and $Mn_2(CO)_{10}$ in order to investigate their effect on graft and homopolymer yields with this heterogeneous system. Preliminary work with acrylic acid and chloroacetylated chitosan did not lead to significant graft yields.[36]

The grafted powdered materials, immediately after reaction completion, were highly swollen in the medium relative to their appearance before grafting. This was expected since the poly(methyl acrylate) (PMA) chains should be grown from the surface and also since PMA is itself soluble in the polymerization medium. Another general observation is that, after each reaction product had been filtered through the thimble and the filtrate was added to excess ether/hexane, no significant polymeric precipitate was observed. This suggests that any homopolymer that was generated was most likely physically entangled within the layer of grafted chains. This is understandable since the major source of homopolymer should be chain transfer from grafted chains.

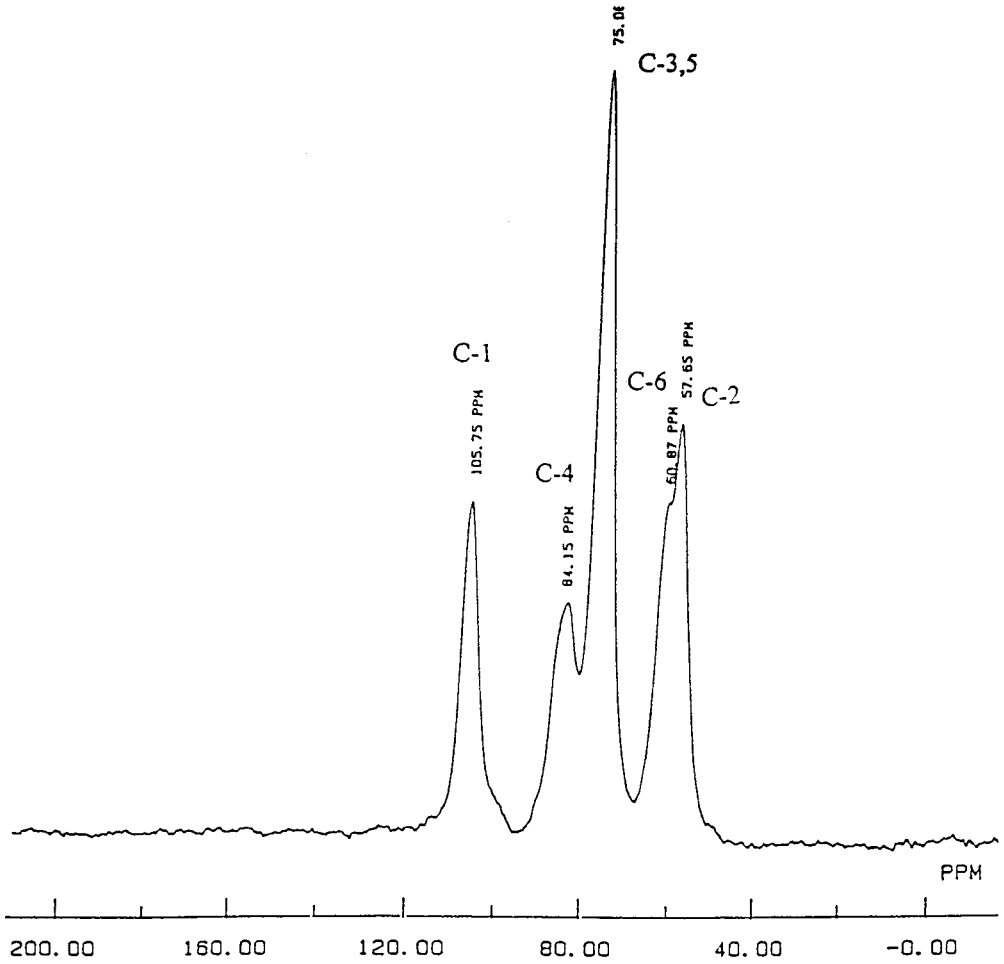
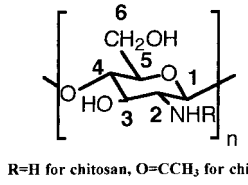


Figure 4. Solid-state CP-MAS ^{13}C NMR spectrum of highly deacetylated chitosan powder.



Carbon	ppm
1	103-106
2	56-57
3	74-75
4	80-85
5	74-75
6	60-62

N-acetyl	ppm
C=O	174-175
CH_3	23-24

Figure 5. Solid-state CP-MAS ^{13}C NMR chemical shifts for chitin and chitosan.[30,31]

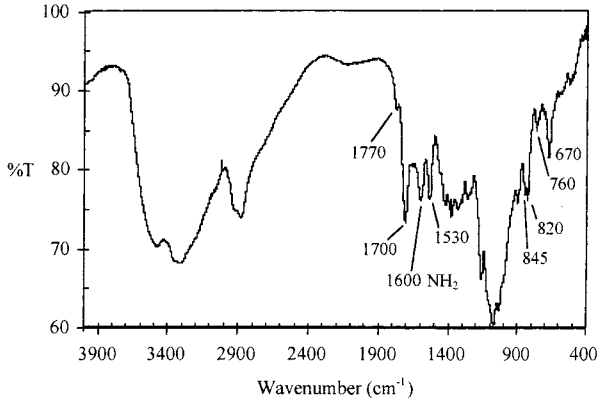


Figure 6. FTIR spectrum of trichloroacetylated chitosan powder.

In an attempt to separate homopolymer from grafted polymer, each product was Soxhlet extracted with acetone for a total of 24 h while intermittently monitoring sample weight (W_4). Generally, none of the samples reached a constant weight over the entire 24 h extraction period. Based on these results, the possible removal of grafted polymer from the extraction thimble was investigated.

The solvent from portions of each acetone extract was evaporated, and the remaining polymer was analyzed for % N content. Small quantities of N were observed for each sample of polymer extract as shown in Table 1. The presence of grafted chitosan in the extract is the only logical source of N for these samples. The classic method for separating homopolymer from graft copolymer is to extract the reaction product with a solvent that is capable of dissolving homopolymer and not trunk polymer. Since acetone is a nonsolvent for chitosan, the removal of grafted chitosan by acetone extractions was rather unexpected. A possible explanation is that when the trichloroacetylated derivative was synthesized, enough of the H-bonded network on the outer portion of particles was disrupted, generating a soluble product once the chitosan was grafted. Since the presence of grafted chitosan appeared to be present with homopolymer in the polymer extract, dried polymer extract samples were dissolved in THF and analyzed with GPC in order to separate graft copolymer from homopolymer. This chromatographic approach is similar to that of McCormick and Park for the characterization of water-soluble dextran-*g*-polyacrylamide.[37] Figure 8 provides the GPC chromatograms for each of the polymer extracts. Generally, each chromatogram shows two major peaks. The highly deacetylated chitosan had a viscosity-

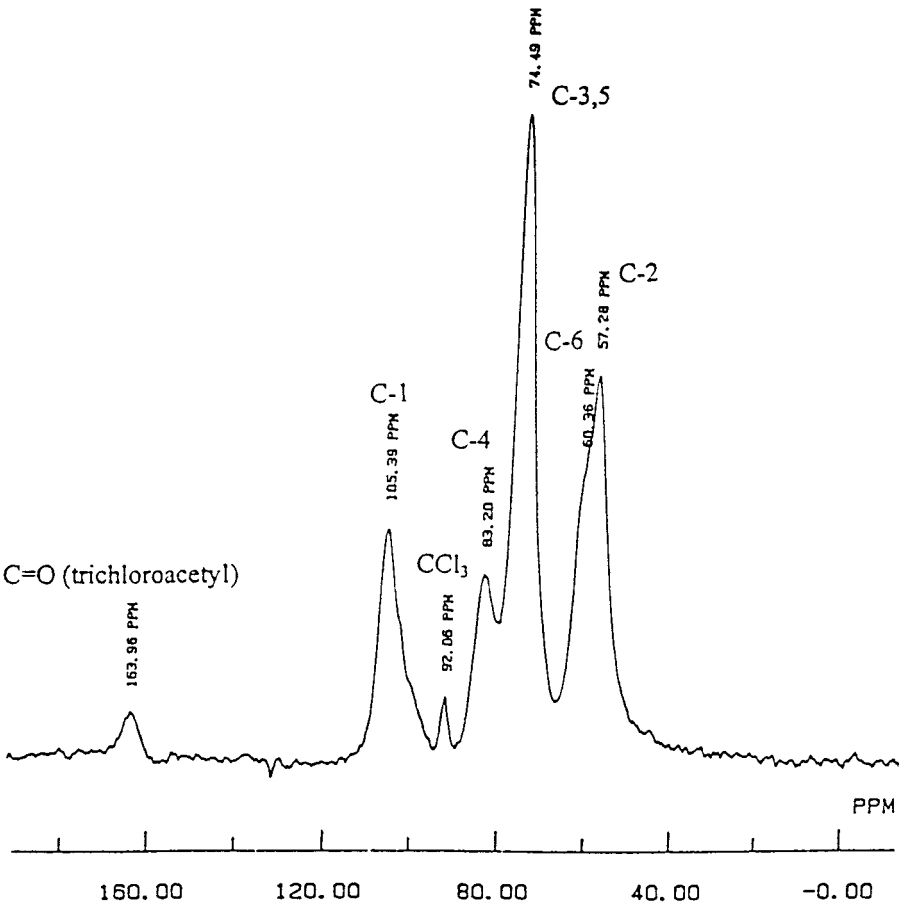


Figure 7. Solid-state CP-MAS ^{13}C NMR spectrum of trichloroacetylated chitosan powder.

Table 1. Graft and Homopolymer Yields for Grafting Experiments Conducted on Trichloroacetylated Chitosan Powder with Methyl Acrylate under Photoinitiating Conditions (436 nm, 25 °C, 30 min)[a]

sample	[methyl acrylate] (mol/L)	$[Mn_2(CO)_{10}]$ (mmol/L)	% N[b] in polym extract	graft frac[c] in polym extract, α	% G[d] yield	% H[e] yield	total % monomer conv
1	3.0	7.2	1.17	0.10	48	37	2.9
2	6.1	7.2	0.48	0.63	199	28	5.1
3	8.3	7.2	0.10	0.77	637	21	10.9
4	6.1	2.8	0.44	0.67	187	23	4.4
5	6.1	5.0	0.45	0.69	191	23	4.6
6	6.1	9.5	0.40	0.77	224	19	5.0

[a] Constant conditions: solvent = ethyl acetate, 4 mL total volume, 40 mg of trichloroacetylated chitosan powder (total trichloroacetyl concentration = 7.2 mM). [b]Weight percent of nitrogen in the polymer which was removed with acetone extraction. [c] The fraction of polymer (removed by acetone extraction) determined to be graft copolymer based on integration of the GP chromatogram (Figure 8). [d]Calculated from eq 3 based on weight of trunk polymer. [e]Calculated from eq 4 based on weight of total poly(methyl acrylate) formed.

average molecular weight of approximately 550 000 g/mol; thus, the larger molecular weight peak is presumably grafted chitosan while the lower molecular weight portion is presumably entirely homopolymer. The general division of grafted polymer and homopolymer is shown in Figure 8. Contrary to the graft copolymer peaks and homopolymer peaks (for samples 3 and 6), homopolymer peaks for samples 1, 2, 4, and 5 are highly multimodal in nature. The molecular weight for most modes are reproducible between samples. The origin of this unusual molecular weight distribution by chain transfer of growing grafted chains to the various transfer agents (monomer and solvent) in the reaction medium would not be expected to yield the observed peaks.

To calculate the overall graft (% G) and homopolymer (% H) for each reaction, the total weight of material removed with acetone extractions was divided into a graft copolymer fraction (α) and a homopolymer fraction (1 − α) as determined by dividing the area under the peak for each fraction by the area under the entire GPC chromatogram. The graft and homopolymer yields shown in Table 1 are based on two major assumptions: the extractions remove all homopolymer from the sample that is contained in the sample, and graft and homopolymer are completely separated by GPC (i.e., there is no high molecular weight homopolymer present in the high molecular weight portion of the chromatogram). It should be noted that the true molecular weight of grafted chitosan is difficult to determine from the data since the column was calibrated with linear PMMA standards. The GPC technique is simply used to separate the different molecular weight species present. The graft yields are observed to increase to over 600% yield with increases in both methyl acrylate and $Mn_2(CO)_{10}$ concentrations. Homopolymer yields tended to fluctuate around 20−30 wt % of total polymer formed. Regardless of the graft and homopolymer yields, the percent

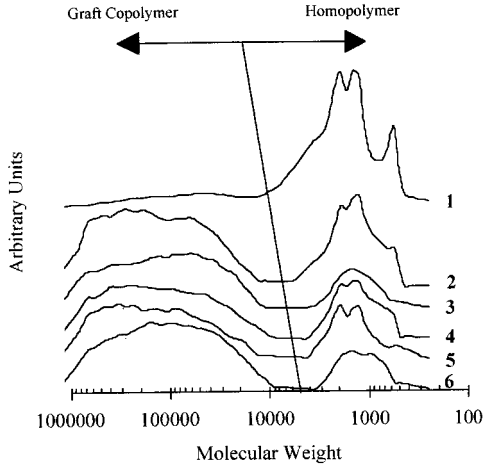


Figure 8. Gel permeation chromatographs for polymer which was extracted with acetone from the grafted sample. Numbers correspond to the samples in Table 1.

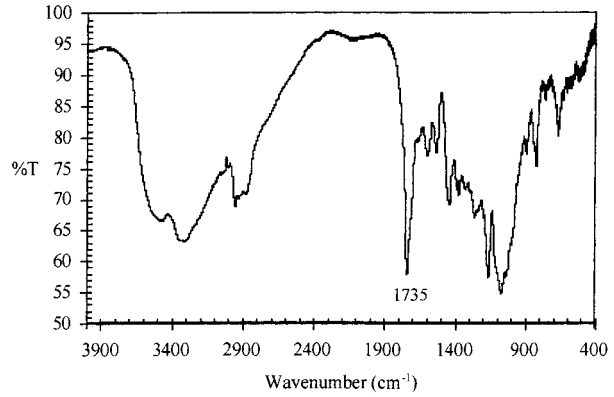


Figure 9. FTIR spectrum of trichloroacetylated chitosan grafted with methyl acrylate under photoinitiating conditions (436 nm, 25 °C) with $Mn_2(CO)_{10}$ (sample 1, Table 1).

monomer conversions for all experiments were in the range of 3−10%. This is not surprising due to the heterogeneous nature of the grafting and to the 30 min reaction time allowed. Compared to concentration changes of $Mn_2(CO)_{10}$, changes in monomer concentration had a greater effect on graft yields. Conditions that increase the rate of propagation were more influential than those which would increase the rate of initiation for the relatively short reaction time.

Further evidence of grafting is shown in Figure 9, which is the IR spectrum of trichloroacetylated chitosan powder grafted with methyl acrylate under photoinitiating conditions with $Mn_2(CO)_{10}$. The absorbance at 1735 cm^{-1} is assigned to the carbonyl side group of poly(methyl acrylate).[32]

There is a possible discrepancy in the data of Table 1 which needs to be discussed. Sample 1 shows the highest % N in the polymer extract; however, it also shows the lowest α relative to the other samples. If these data do not truly provide an accurate representation of graft and homopolymer yields, the potential reason could be based on the solubility of the graft copolymer. With portions of the grafted chitosan being removed with acetone extractions and subsequent GPC analysis conducted with THF, if the graft copolymer is less soluble in THF (relative to acetone based on polarity considerations), portions of graft copolymer could be removed by sample filtration before injection and thus decrease the true graft fraction α observed in the chromatogram. Sample 1 would be most effected by this since it presumably has the lowest % G based on the relatively low monomer concentration employed for grafting.

Conclusions

Chitosan powder was successfully heterogeneously grafted with methyl acrylate utilizing the trichloroacetyl/$Mn_2(CO)_{10}$ photoinitiating system as outlined in Figure 1. This system promotes specific macroradical formation since trichloroacetyl groups were successfully bonded to the chitosan backbone; however, homopolymer was still observed in all experiments (presumably from the chain transfer of growing grafted chains). The initial separation of graft and homopolymer was performed by means of Soxhlet extraction with acetone. Removal of surface grafted chitosan was observed during acetone extractions. The polymeric extract was dried, redissolved in THF, and analyzed with GPC. Chromatograms were observed to have a high molecular weight region (assumed to be grafted chitosan) and a low molecular weight region (assumed to be homopolymer). Graft and homopolymer yields were obtained by monitoring product weights (of both polymer formed during the reaction and polymer removed with extraction) and the relative amounts of graft and homopolymer in the polymer extract as determined by GPC. Grafting yields achieved levels above 600% (based on weight of trunk polymer) while homopolymerization was observed to be on the order of 20−30% based on total weight of polymer formed.

Acknowledgment. The authors thank Dr. S. Sankar of the NCSU Chemistry Department for solid-state NMR training. Suggestions for improving the manuscript provided by Dr. S. Purrington (Chemistry Department, NCSU) and Dr. A. Tonelli (TECS Department, NCSU) are greatly appreciated. Helpful discussions with Dr. A. Schreiner (Chemistry Department, NCSU) concerning manganese carbonyl mechanisms is gratefully acknowledged. The authors thank the USDA/CSREES Program, Grant 9701669, for funding this work.

References and Notes

(1) Muzzarelli, R. *Chitin*; Pergamon: New York, 1977.
(2) Rathke, T. D.; Hudson, S. M. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34* (3), 375.
(3) Kurita, K. In *Applications of Chitin and Chitosan*; Goosen, M. F. A., Ed.; Technomic: Lancaster, 1997; p 297.
(4) Li, W.; Li, Z.; Liao, W.; Feng, X. *J. Biomater. Sci., Polym. Ed.* **1993**, *4* (5), 557.
(5) Caner, H.; Hasipoglu, H.; Yilmaz, O.; Yilmaz, E. *Eur. Polym. J.* **1998**, *34* (3/4), 493.
(6) Kim, K. H.; Kim, K. S.; Shin, J. *Polymer (Korea)* **1987**, *11* (2), 133.
(7) Shantha, K. L.; Bala, U.; Rao, K. P. *Eur. Polym. J.* **1995**, *31* (4), 377.
(8) Lagos, A.; Reyes, J. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 985.
(9) Yazdani-Pedram, M.; Lagos, A.; Retuert, J.; Guerrero, R.; Riquelme, P. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32* (5), 1037.
(10) Retuert, J.; Yazdani-Pedram, M. *Polym. Bull. (Berlin)* **1993**, *31*, 559.
(11) Shigeno, Y.; Kondo, K.; Takemoto, K. *J. Macromol. Sci., Chem.* **1982**, *A17* (4), 571.
(12) Singh, D. K.; Ray, A. R. *J. Appl. Polym. Sci.* **1994**, *53*, 1115.
(13) Singh, D. K.; Ray, A. R. *J. Appl. Polym. Sci.* **1997**, *66*, 869.
(14) Blair, H. S.; Guthrie, J.; Law, T.; Turkington, P. *J. Appl. Polym. Sci.* **1987**, *33*, 641.

(15) Takahashi, A.; Sugahara, Y.; Horikawa, Y. *Sen-I Gakkaishi* **1987**, *43* (7), 362.
(16) McDowall, D. J.; Gupta, B. S.; Stannett, V. T. *Prog. Polym. Sci.* **1984**, *10*, 1.
(17) Bamford, C. H. In *Reactivity Mechanism and Structure in Polymer Chemistry*; Jenkins, A. D., Ledwith, A., Eds.; Wiley: London, 1974; p 52.
(18) Bamford, C. H. In *Comprehensive Polymer Science*; Allen, G., Aggarwal, S. L., Russo, S., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 3, p 123.
(19) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.
(20) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; p 196.
(21) Rosa, A.; Ricciardi, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1996**, *35*, 2886.
(22) Bamford, C. H.; Dyson, R. W.; Eastmond, G. C. *J. Polym. Sci., Part C* **1967**, *16*, 2425.
(23) Bamford, C. H.; Dyson, R. W.; Eastmond, G. C.; Whittle, D. *Polymer* **1969**, *10*, 759.
(24) Bamford, C. H.; Eastmond, G. C.; Whittle, D. *Polymer* **1969**, *10*, 771.
(25) Bamford, C. H.; Dyson, R. W.; Eastmond, G. C. *Polymer* **1969**, *10*, 885.
(26) Muzzarelli, R. In *The Polysaccharides*; Aspinall, G., Ed.; Academic Press: New York, 1985; Vol. 3, p 417.
(27) Salmon, S. Ph.D. Thesis, North Carolina State University, Dec 1995.
(28) Wang, W.; Bo, S.; Li, S.; Qin, W. *Int. J. Biol. Macromol.* **1991**, *13*, 281.
(29) Brimm, E. O.; Lynch, M. A.; Sesny, W. J. *J. Am. Chem. Soc.* **1954**, *76*, 3831.
(30) Saito, H.; Tabeta, R.; Ogawa, K. *Macromolecules* **1987**, *20*, 2424.
(31) Hirano, S.; Sakaguchi, T.; Kuramitsu, K. *Carbohydr. Polym.* **1992**, *19*, 135.
(32) *The Aldrich Library of Infrared Spectra*; Pouchert, C. J., Ed.; Aldrich Chemical Company: Milwaukee, WI, 1981.
(33) Tanaka, H.; Azuma, C.; Sanui, K.; Ogata, N. *Polym. J.* **1980**, *12*, 63.
(34) *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, 1st ed.; Pouchert, C. J., Behnke, J., Eds.; Aldrich Chemical Co.: Milwaukee, WI, 1993.
(35) Kurita, K.; Chikaoka, S.; Kamiya, M.; Koyama, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 927.
(36) Jenkins, D. W. M.S. Thesis, North Carolina State University, Dec 1997.
(37) McCormick, C. L.; Park, L. S. *J. Appl. Polym. Sci.* **1981**, *26*, 1705.

MA011336B