

Microwave Assisted Graft Copolymerization of N-Isopropyl Acrylamide and Methyl Acrylate on Cellulose: Solid State NMR Analysis and CaCO_3 Crystallization

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Summary: Graft copolymerization of N-isopropyl acrylamide and methyl acrylate on α -cellulose was carried out under microwave irradiation at specific cut off temperatures with cerium (IV) ammonium nitrate and potassium persulfate (KPS) as the initiating system. The role of KPS was to oxidize Ce (III) to Ce (IV) which is the active species in radical formation. The reactions at a temperature cut off of 60 °C were confirmed by ^{13}C nuclear magnetic resonance cross-polarization with magic-angle spinning (^{13}C NMR CP/MAS) and Fourier-transform infrared spectroscopy (FTIR). The extent of grafting was calculated from weight gain and ^{13}C resonances. The grafted cellulose was thermally more stable than the parent cellulose. An attempt to do grafting at a higher cut off temperature of 80 °C was made, however, no grafting was observed from ^{13}C NMR CP/MAS but TGA results showed that a cellulose having more thermal stability resulted which was attributed to cross linking. Crystallization of CaCO_3 was carried out using the grafted materials as templates showed better nucleation and different crystal structure was observed.

Keywords: ^{13}C NMR P/MAS; crystallization; FT-IR; graft copolymers; nucleation

Introduction

Cellulose is one of the most abundant naturally occurring polysaccharides consisting of glucose units joined together by β -1-4 linkages. The extensive hydrogen bonding that exists between the chains renders it highly crystalline and resistant to dissolution by normal organic solvents. Thus, most grafting reactions are done in a heterogeneous system where the cellulose fibers are swollen by solvent. A wide range of vinyl monomers can be grafted on cellulose to produce a wide range of biodegradable materials with different chemical and

physical properties. Cellulose and cellulosic materials have applications in the paper, food, paint & pharmaceutical industries.

Grafting of cellulose and other polysaccharides can be initiated by various transition metal ions such as Fe^{+3} , Cu^{+2} , Ce^{+4} e.t.c. via free radical initiation.^[1] Grafting of cellulose and its derivatives initiated by ceric (IV) ion has been widely studied.^[2–11] The mechanism of initiation is through the formation of free radicals directly on the cellulose backbone by cleaving the C2-C3 bond^[12,13] and oxidation of cellulosic chain ends containing hemiacetal linkages.^[14] Furthermore it has been suggested that the Ce^{+4} ions can also abstract protons from the hydroxyl groups of these polysaccharides thereby facilitating grafting resulting in the formation of ether linkages.^[13,15] The Ce^{+4} can also form radicals on the monomer and this results in homopolymer formation. Recently it has been

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shown that the addition of certain alcohols to Ce^{+4} initiated grafting of cellulose resulted in a higher percentage grafting as well as improved grafting efficiency.^[3] A double initiating system termed Ce^{+4} -KPS has been successfully used in grafting copolymerization of diallyldimethyl ammonium chloride (DADMAC) and acrylamide on starch.^[16] The inclusion of KPS in Ce^{+4} initiated reactions was shown to improve the percentage grafting, by oxidation of Ce^{+3} to Ce^{+4} , which is the active specie in grafting reactions. Grafting of itaconic acid on cellulose was also done using KPS as initiator and the mechanism of radical formation on cellulose backbone was explained to be via proton abstraction by initiator radicals.^[17]

Microwave assisted grafting of chitosan^[18] and guar gum^[19] has been carried out with and without the redox system $AgNO_3$ /KPS/ascorbic acid. Microwave activation was also used in homogeneous esterification of cellulose.^[20,21] The use of microwave in grafting reactions provided shorter reaction times compared to conventional methods.

In this study, we tested a combination of double initiating system (Ce^{+4} -KPS) under microwave irradiation on graft copolymerization of NIPAM and MA. Thus a series of reactions were done varying the microwave power as well as the reaction temperature to determine their effect on grafting of α -cellulose. We also studied the crystallization of calcium carbonate using the grafted α -cellulose as template.

Experimental Part

Materials

Methyl acrylate (MA) (Aldrich) was purified by first extracting stabilizers with aqueous sodium hydroxide 0.3 M and dried over magnesium sulfate, vacuum distilled and stored below 5 °C. N-isopropyl acrylamide (NIPAM) (Sigma) was recrystallized from methanol and stored below 5 °C, Cerium (IV) ammonium nitrate (CAN) (Fluka) and Potassium persulfate (KPS)

(Aldrich) were used as received. α -Cellulose (α -CE) was washed with water then ethanol and vacuum dried to a constant weight at 60 °C. Nitric acid 55 % (R & S Enterprises) was used as received.

Grafting Procedure

In a typical reaction, α -cellulose (0.5 g, 3.08×10^{-3} moles of anhydroglucose unit) was dispersed in 100 ml of 2.5×10^{-3} M HNO_3 and CAN (0.025 g, 9.5×10^{-5} moles) was added then stirred for 30 minutes. The two monomers (total moles 5.0×10^{-3} and mole ratio MA: NIPAM=1) were then added whilst vigorously stirring. The microwave oven was set at appropriate microwave power (MWP), temperature and run time of 10 minutes. At the end of the reaction, the products were precipitated from a mixture of water and methanol. The homopolymers were extracted with water/THF mixture. The resulting graft copolymer was then dried to constant weight and the percentage grafting (% G) was calculated. The graft copolymers (α -CE-g-NIPAM-co-MA) are referred as G1, G2, and G3 in order of increasing % grafting.

Crystallization of $CaCO_3$

The grafted materials were then used as templates for $CaCO_3$ crystallization. In a typical reaction, 0.025 g of α -cellulose or grafted α -cellulose was dispersed in 15 ml of 0.025 M $CaCl_2$ solution for 2 hrs after which 15 ml of 0.025 M Na_2CO_3 solution was added slowly whilst stirring. The pH was adjusted to neutral. After 24 hrs, the reaction was stopped and the product filtered through a 0.22 micron membrane filter paper. The harvested $CaCO_3$ and α -cellulose fiber were then dried and analyzed by scanning electron microscopy (SEM) and FT-IR.

Analysis

Gravimetric Analysis

The weight of the grafted cellulose after homopolymer extraction was used to

calculate the % G using the following equation:

$$(\%G) = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

Where W_1 and W_0 denote the weight of the grafted α -cellulose and the weight of the original α -cellulose respectively.

CP/MAS ^{13}C NMR

The anomeric and carbonyl ^{13}C NMR peak intensities were used to estimate the % G. The ^{13}C intensities from CP/MAS are not quantitative because the peak intensities depends on the rate of cross polarization which is usually different for different carbon atoms.^[22] Thus direct integration of ^{13}C peaks of different carbon nuclei type may give misleading peak ratios. In order to quantify using ^{13}C peak intensities, the following equation was used.^[23]

$$\frac{S(\tau)}{S_o} = \frac{1}{\lambda} \left[1 - \exp\left(\frac{-\lambda\tau}{T_{IS}}\right) \right] \exp\left(\frac{-\tau}{T_{1\rho}(^1H)}\right), \quad (2)$$

$$\lambda = 1 + \frac{T_{IS}}{T_{1\rho}(^{13}\text{C})} - \frac{T_{IS}}{T_{1\rho}(^1H)} \quad (3)$$

Where S_o is the “true” area of resonance; $T_{1\rho}(^1H)$ and $T_{1\rho}(^{13}\text{C})$ are the proton and carbon spin lattice relaxation times in the rotating frame and T_{IS} is the cross relaxation time between protons and carbon. By fitting the experimental data obtained from a plot of area of resonance of both the anomeric carbon and carbonyl carbon versus contact time (Figure 1) to Equation (2), S_o and $T_{1\rho}(^1H)$ for the three graft copolymers were calculated.

From the ^{13}C CP/MAS spectra, there are two side bands [SB1 (A) and SB2 (C)] which are due to the anomeric carbon. The two side bands were also used in the calculation with an assumption that the carbonyl carbon relaxation data is the same for the side bands as in the main carbonyl peak.

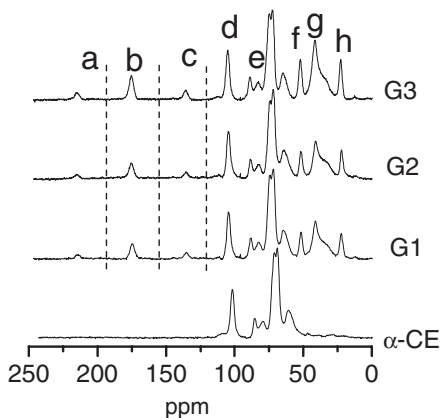


Figure 1.

^{13}C CP-MAS NMR spectra of α -CE and the graft copolymers G1, G2 and G3. a) and c) carbonyl side bands, b) carbonyl peak, d) Anomeric carbon, e) C2-C6 of cellulose, f) CH_3 carbon peak of MA, g) the carbon peaks of the grafted copolymer (NIPAM-co-MA), h) $2 \times \text{CH}_3$ carbons of NIPAM.

The % G was then calculated using the following equation

Corrected NMR % grafting

$$= \frac{S_o(T)}{S_o(T) + S_o(D)} \times 100 \quad (4)$$

and

$$S_o(T) = S_o(A) + S_o(B) + S_o(C) \quad (5)$$

Where $S_o(T)$ is the sum of the true area of resonance $S_o(A \rightarrow C)$ with B denoting the main peak of the carbonyl carbon whilst A and C denoting the side bands SB1 and SB2 respectively and $S_o(D)$ is the true area of resonance for the anomeric carbon.

However, besides using the corrected areas of resonance of the carbon peaks, direct integration of the ^{13}C peaks was made and the ratio of the carbonyl peaks (main peak and the side bands) to the anomeric carbon of α -cellulose was used to calculate % G and the results were compared to that of weight loss as well.

FT-IR Spectroscopy

A Perkin Elmer FT-IR transmission spectrophotometer ranging from 400–4500 cm^{-1} was used. KBr was used to prepare the sample disc for analysis.

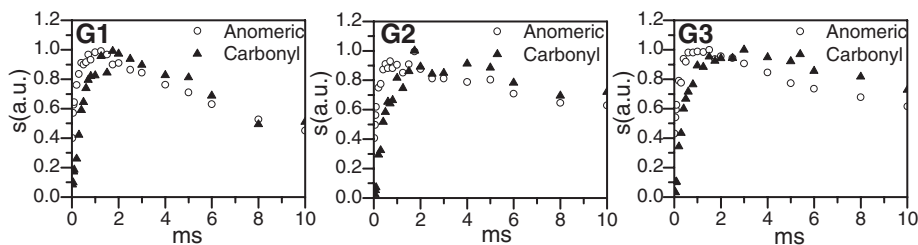


Figure 2.

Correlation between area of resonance C1 (Anomeric carbon) of α -cellulose and the area of resonance C* (NIPAM/MA) of the two monomers used and the contact time for the three graft copolymers G1, G2 and G3.

Thermogravimetric Analysis (TGA)

The thermogravimetric curves for all the samples were obtained from a Shimadzu analyzer with a heating rate of 10 °C per minute.

Results and Discussion

The use of microwave irradiation on Ce^{+4} -KPS initiated grafting of cellulose was carried out successfully with the reaction times reduced to 10 minutes. The peaks due to different carbon nuclei are shown in Figure 1. The carbonyl peaks (a, b and c) and the anomeric peak (d) were used to calculate % G whilst the MA peak (f) and the NIPAM peak (h) were used to estimate the % incorporation of each monomer in the graft copolymer.

In order to correlate the intensities of the anomeric carbon and carbonyl carbon peaks, the proton and carbon spin-lattice relaxation times were determined. A series of spectra were carried out with the contact time ranging from 0 to 12 ms and are shown in (Figure 2). The proton relaxation times measured on the anomeric carbon and carbonyl carbon were rather similar

(Figure 2) meaning that the system can be treated as homogeneous.^[8]

The % G calculated by i) direct integration of ^{13}C NMR peaks and ii) correction of the area of resonance of the ^{13}C CP/MAS peaks gave results that were similar to those calculated from gravimetric method. This showed that solid state NMR can be used to estimate % G of α -cellulose. The % incorporation of each monomer was also estimated from CP/MAS spectra and that MA incorporation was much higher than that of NIPAM (Table 1). This is expected as MA has higher reactivity than NIPAM. The microwave power had no effect on percentage incorporation of the monomers and small effect on % G. The FT-IR spectra (Figure 3) show the MA and NIPAM carbonyl absorption peaks of the grafted copolymers polymers at 1736 and 1650 cm^{-1} respectively.

The TGA curves, Figure 4, show an increase in thermal stability with an increase in percentage grafting.

Analogous reactions at temperature cut-off at 80 °C of grafting α -cellulose with NIPAM and MA showed that there was no grafting from solid state NMR (Figure 5).

Table 1.

A comparison of the %G as calculated from three different methods as well as the % incorporation of each monomer.

Sample	MWP (W)	Carbonyl	SB1	SB2	Anomeric	%G	%G	%G	%MA	%NIPAM
						CP/MAS	Calc.	(WG)	(mol)	(mol)
G3	800	28.33	9.68	11.13	50.86	49.14	48.88	55.01	66	34
G2	600	20.65	7.82	8.81	62.71	37.29	38.42	42.12	64	36
G1	400	20.65	7.25	8.2	63.9	36.86	36.56	38.31	67	33

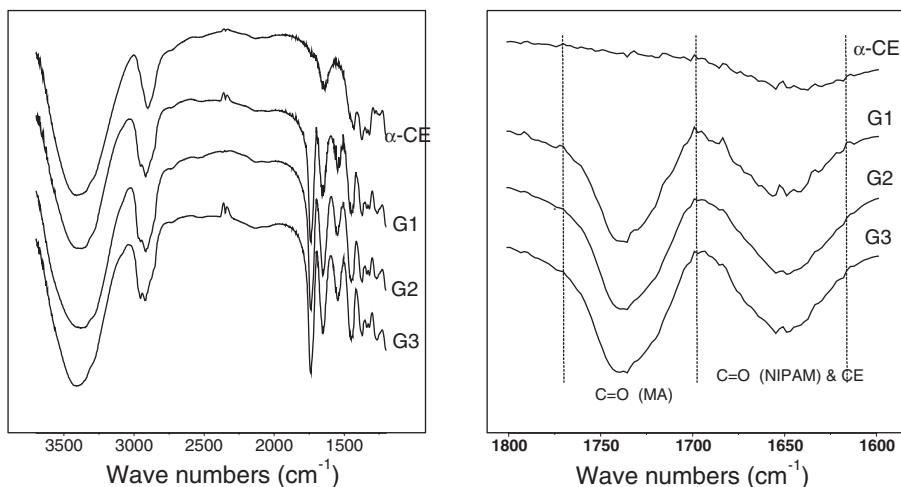


Figure 3.

A comparison of the FT-IR spectra of α -CE and the graft copolymers G1, G2 and G3 showing the carbonyl peaks due to the grafted polymers.

The NMR results showed that there was no polymer grafted on α -cellulose as the ^{13}C peaks of the polymer were absent. The carbonyl peak of the polymers was not observed in FT-IR spectra as well. However, the results from TGA showed an increase in thermal stability of the grafted materials which is typical for grafted materials as illustrated in (Figure 5). The reason for having an increase in the thermal stability of cellulose materials is suggested

to be due to the cross linking of cellulose. In previous studies of conventional cerium initiation, a decrease in %G and an increase in homopolymer formation as temperature was increased to 60°C was observed.^[2,6] We concluded that the Ce^{+4} -KPS initiation system is not suitable for microwave reactions above 60°C temperature cut off as only homopolymer is formed and cross linking is highly enhanced. The presence of a water soluble initiator KPS can also

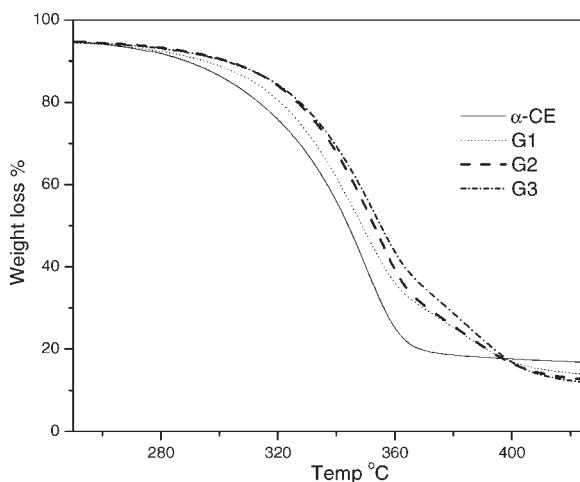


Figure 4.

TGA curves of α -CE and the graft copolymers G1, G2 and G3 showing an increase in thermal stability with % grafting.

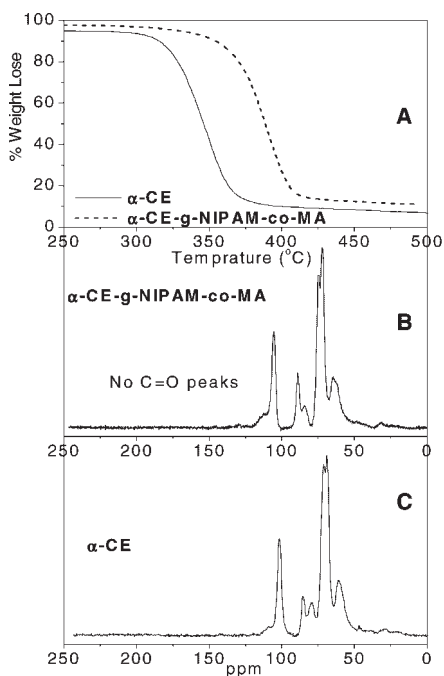


Figure 5.

A) TGA curves of α -CE and α -CE grafted with NIPAM showing the thermally more stable ungrafted material. C and B) ^{13}C NMR of α -CE and α -CE grafted with NIPAM and MA (α -CE-g-NIPAM-co-MA) respectively.

contribute to homopolymer formation rather than grafting at these high temperatures.

The crystallization of calcium carbonate results showed that the grafted cellulose can nucleate CaCO_3 crystal formation much better than ungrafted cellulose. Crystals formed in the presence of cellulose were rhombohedral single crystals whereas platelet like crystals that stacked together and cubical single crystals were formed in the presence of grafted materials.

Grafting can also aid the adsorption of these crystals on the surface of the fiber as many particles were adsorbed on the surface of the grafted fibers. However, there was no effect of % G on size and morphology of crystals of CaCO_3 . Calcium carbonate exists in three polymorphs: vaterite, aragonite and calcite in order of their thermodynamic stability and phase transformation possible.

From infrared spectroscopy, Figure 7, the peaks at 876 cm^{-1} and 711 cm^{-1} are due the calcite.^[24] The absence of aragonite and vaterite polymorphs' characteristic peaks at 1057 cm^{-1} ^[25] and 745 cm^{-1} ^[24] respectively means that the synthesized

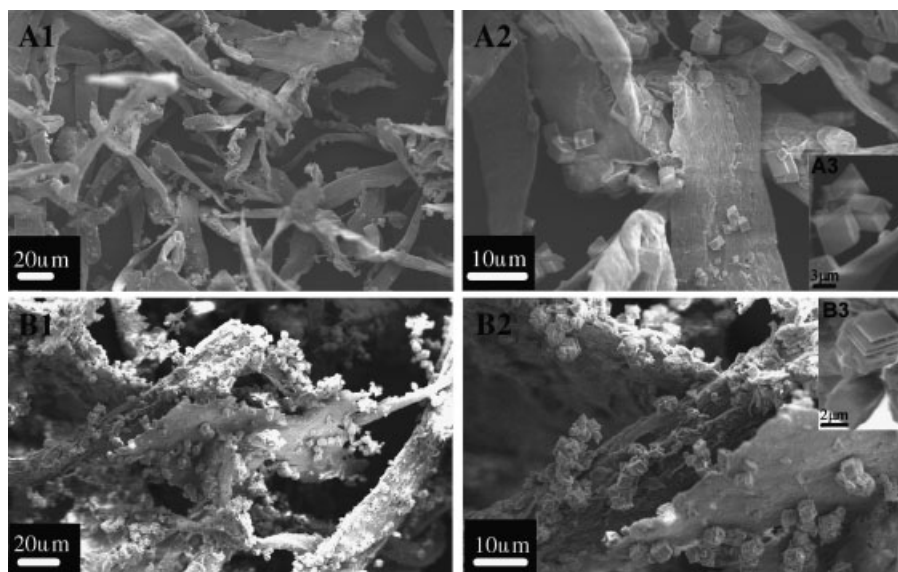


Figure 6.

SEM images of CaCO_3 crystals synthesized in the presence of A) alpha cellulose and B) CE grafted copolymerized with NIPAM with MA (G2). A2, A3, B2 and B3 are enlargements.

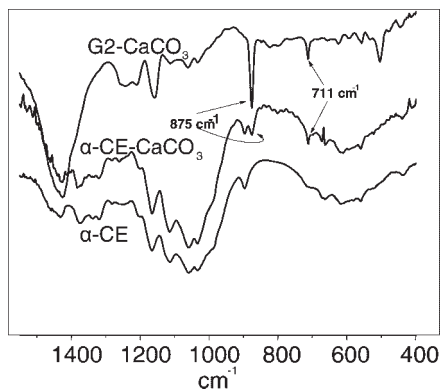


Figure 7.

A comparison of the FT-IR spectra of α -CE, α -CE- CaCO_3 and the graft copolymer G2- CaCO_3 showing the peaks due to the calcite and vaterite.

CaCO_3 consisted of mainly the calcite polymorph.

Conclusion

Grafting of cellulose was confirmed by solid state NMR, FT-IR as well as thermogravimetric analysis. The % G calculated from ^{13}C NMR correlated well with % grafting calculated from weight gain. It was found that microwave irradiation of cerium initiated grafting of cellulose is limited to temperatures lower than 60°C with higher temperatures resulting in cross linking of the celluloses as concluded from TGA curves and ^{13}C NMR spectra. The reaction times in microwave assisted grafting were reduced significantly and the effect of microwave irradiation power on % grafting was less significant. The grafted cellulose materials had better nucleating properties than cellulose as more crystals were formed on the surface of the fiber. The crystal morphology was different although the crystal sizes were relatively similar.

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