

Microwave Promoted Synthesis of Chitosan-Graft-Poly(acrylonitrile)

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ABSTRACT: Using microwave (MW) irradiation, polyacrylonitrile was grafted onto chitosan with 170% grafting yield under homogeneous conditions in 1.5 min in the absence of any radical initiator or catalyst. Under similar conditions a maximum grafting of 105% could be achieved when the $K_2S_2O_8$ /ascorbic acid redox system was used as radical initiator in a thermostatic water bath at $35 \pm 2^\circ\text{C}$. The representative graft copolymer was characterized by Fourier transform infrared spectra, thermogravimetric analysis, and X-ray diffraction measurement, taking chitosan as a refer-

ence. The effects of such reaction variables as monomer/chitosan concentration, MW power, and exposure time on the graft copolymerization were studied. A probable mechanism for grafting without the redox system under microwaves was proposed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 820–825, 2005

Key words: chitosan-grafted-polyacrylonitrile; microwave irradiation; $K_2S_2O_8$ /ascorbic acid

INTRODUCTION

Chitosan obtained from chitin poly- β -(1 \rightarrow 4)-*N*-acetyl-D-glucosamine through deacetylation using strong aqueous alkali solution is a more versatile form of this polysaccharide, which is the second most abundant natural polymer on earth after cellulose. Chitosan-*g*-poly (glycidylmethacrylate) copolymer was used for immobilization of urease¹ and other modifications such as the grafting of methylmethacrylate onto chitin initiated by tributylborane,² poly (3-hydroxyalkonate)-chitosan conjugates,³ chitosan modified poly(glycidylmethacrylate-butylacrylate), and chitosan grafted bovine pericardial tissue-anticalcification properties have been studied.⁴ However, modification of chitosan via grafting of vinyl monomers is one of the most effective methods to incorporate desirable properties into chitosan without sacrificing its biodegradable nature. There has been growing interest in the grafting of vinyl monomers onto chitosan for medical and biomedical applications.^{5–12} Many graft copolymers of chitosan and vinyl monomers were synthesized and evaluated as flocculents, paper strengtheners, drug-releasers, and so on.^{13–19} Con-

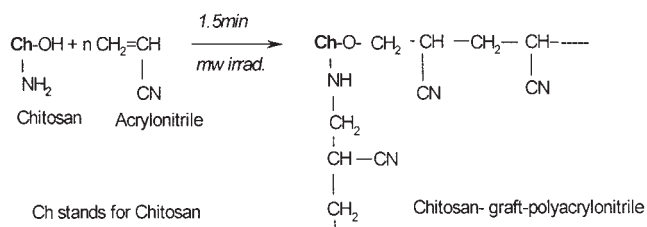
ventionally vinyl monomers are grafted onto chitosan using various redox systems.^{20–23} Concurrent homopolymer formation is the main constraint in graft copolymerization, leading to low grafting yield. Microwave irradiation²⁴ as an efficient thermal energy is becoming standard technique in various fields of chemistry. Grafting of butylacrylate,²⁵ acrylic acid,²⁶ and acrylonitrile²⁷ onto starch, grafting of acrylamide onto low-density polyethylene (LLDPE) films,²⁸ and grafting of butyl methacrylate onto wool fibers²⁹ was studied recently under microwave irradiation. Methylmethacrylate was very recently polymerized³⁰ under microwave with a very low concentration of the initiators and grafting of polyacrylonitrile³¹ and polyacrylamide³² onto guar gum was successfully achieved under microwaves without any catalyst and redox initiators. In the present article we report on the synthesis of Ch-*g*-PAN in 170% grafting yield under microwaves without using any initiator or catalyst in a very short reaction time while the same could be synthesized only in 105% yield using $K_2S_2O_8$ /ascorbic acid as redox initiator in a thermostatic water bath in 1 h.

EXPERIMENTAL

A Kenstar (Model No. MOW 9811, 1200 W) domestic microwave oven was used for all experiments. The average bulk temperature at the end of the reaction was measured by inserting a thermometer into the reaction mixture. The temperature was less than 100°C because the all the reactions were performed

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Scheme 1

in aqueous medium. Infrared (IR) spectra were recorded on a Bruker Vector-22 infrared spectrophotometer using KBr pellets. A sample of pure chitosan (Sigma) from crab shells was used; the degree of deacetylation was 85%. Chitosan was ground to fine powder (>140 mesh) from flats and dried under a vacuum at room temperature. Commercial chitosan was purified by dissolution in acetic acid and separation in alkaline solution and then extraction in a soxhlet apparatus by refluxing in alcohol for 24 h and drying at 60°C in vacuum for 48 h before use. Acrylonitrile (Merck) was distilled in a stream of nitrogen before use. Ascorbic acid and potassium persulfate (BDH, Analar grade) were used without further purification. X-ray diffraction (XRD) was carried out on an Isodebexlex 2002 X ray powder diffractometer and thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 6TGA in N₂ atmosphere. A sample with maximum grafting yield was selected for characterization by spectral studies.

The percentage and efficiency of grafting were calculated according to Kojima et al.,³³

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

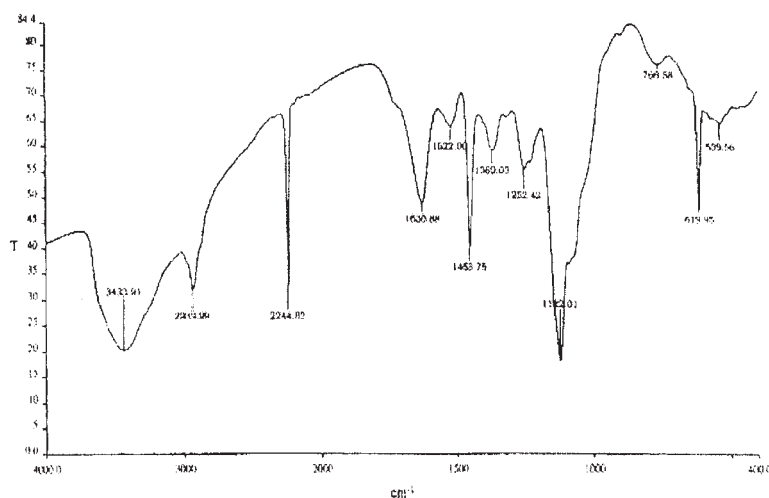
$$\% \text{ efficiency (\%E)} = \frac{W_1 - W_0}{W_2} \times 100 \quad (2)$$

where W_1 , W_0 , and W_2 denote, respectively, the weight of the grafted chitosan, the weight of original chitosan, and the weight of the monomer used.

Graft copolymerization

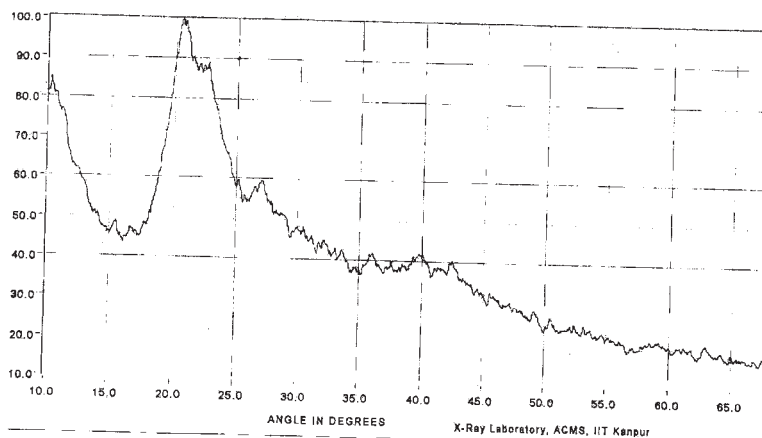
Grafting using redox initiator under thermostatic water bath

To a solution of chitosan (0.1 g) in 25 mL of 5% aqueous formic acid, acrylonitrile (26×10^{-2} mol/L) and ascorbic acid (2.3×10^{-2} mol/L) were added and thermostated in a water bath at $35 \pm 2^\circ\text{C}$. After 30 min $\text{K}_2\text{S}_2\text{O}_8$ (1×10^{-3} mol/L) was added and this time of the addition of persulfate was taken as zero time. Graft copolymerization was allowed for 1 h. Then the reaction product was precipitated out with 2 vol of isopropanol, filtered, washed with distilled water to remove the unmodified soluble low-molecular-weight chitosan,³⁴ and dried. It was again subjected to soxhlet refluxing for 8–12 h using *N,N*-dimethylformamide (DMF) to solubilize and remove the homopolymer; percentage grafting and

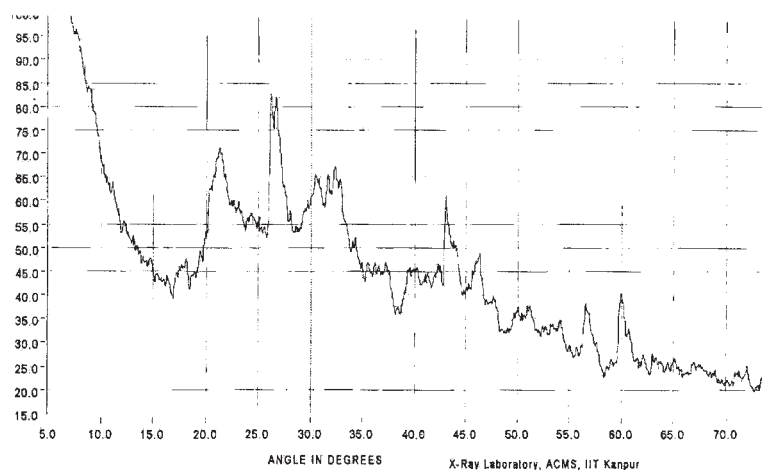


IR of Ch-g-PAN

Figure 1 IR of Ch-g-PAN.



XRD Chitosan



XRD Ch-g-PAN

Figure 2 (Top) XRD of chitosan. (Bottom) XRD of Ch-g-PAN.

percentage efficiency were calculated (%G = 105 and %E = 30.5%).

Grafting under microwave irradiation

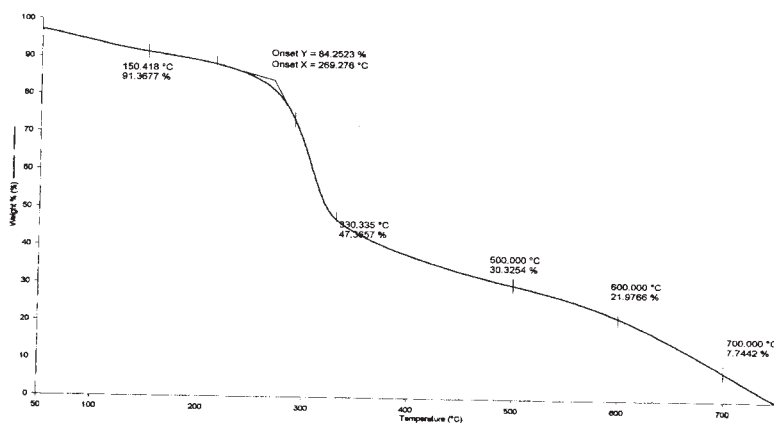
Chitosan (0.1 g), dissolved in 25 mL of 5% aqueous formic acid (v/v) and acrylonitrile (26×10^{-2} mol/L), was irradiated in a domestic microwave oven in a 150-mL flask. The reaction was repeated with a different monomer concentration in the range of 10 – 28×10^{-2} mol/L, microwave (MW) power, and exposure time. Chitosan-g-polyacrylonitrile (Ch-g-PAN) was separated from PAN as in the above method. The percentage of grafting and grafting efficiency were calculated. The maximum %G

achieved was 170% with efficiency of 49.41%. The reaction was studied for different microwave power and exposure time and optimal grafting was observed at 80% MW power at 95°C in 1.5 min (Scheme 1).

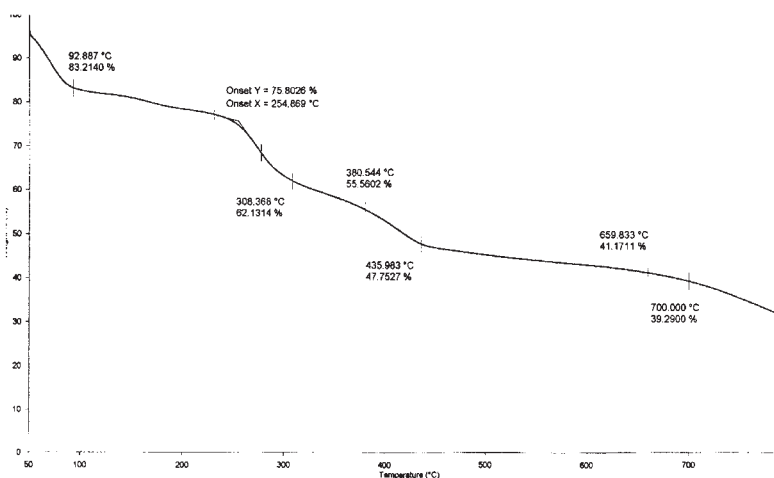
RESULTS AND DISCUSSION

Characterization of the grafted chitosan

Graft copolymer based on chitosan was synthesized by grafting acrylonitrile onto a polysaccharide molecule in aqueous medium using microwave radiation. The grafting was confirmed by comparing the IR spectra of chitosan with that of the grafted product (Fig. 1).



TGA Chitosan



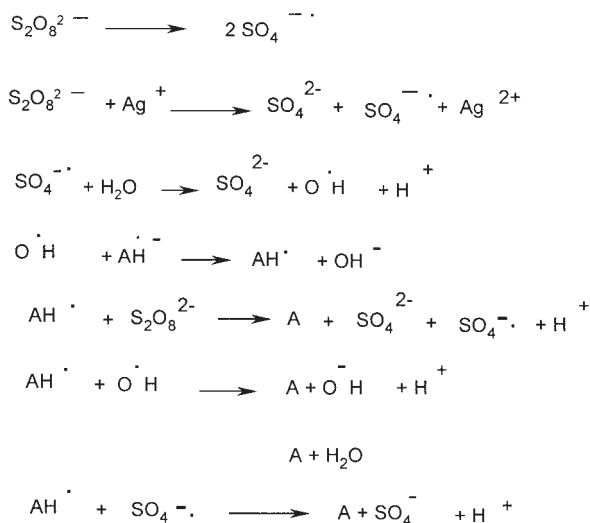
TGA Ch-g-PAN

Figure 3 (Top) TGA of chitosan. (Bottom) TGA of Ch-g-PAN.

The IR spectrum of the chitosan showed strong peaks at 1030, 1076, and 1261 cm^{-1} , characteristic peaks of a saccharide structure (due to O-H bending, C-O stretching, and C-N stretching). The strong peak around 3400 cm^{-1} could be assigned to the stretching vibration of O-H, the extension vibration of N-H, and interhydrogen bonds of the polysaccharide. The appearance in Ch-g-PAN of -CN (nitrile) absorption at around 2244 cm^{-1} and the CH_2 deformation vibration at around 1453 cm^{-1} confirmed the grafting. At 2830, 2927, and 2716 cm^{-1} peaks are observed due to C-H stretching bands at $-\text{CH}_2-\text{CN}-$, $-\text{CH}_2-$, and $-\text{CH}-$, respectively, at grafted chains. An intense peak of methylene C-H bending (of grafted chains) at 1364 cm^{-1}

further supports the grafting. Peaks at 1030 and 1076 cm^{-1} due to C-O and O-H stretching, respectively, are reduced in intensity with respect to chitosan due to appreciable grafting at these sites.

The grafting was also supported by XRD (Fig. 2) and TGA (Fig. 3). It is obvious that the X-ray diffraction spectra of the grafted chitosan show more crystalline areas (due to grafted polyacrylonitrile chains) than the chitosan itself, while the original crystalline peak of chitosan is decreased in height. TGA analysis also confirms the grafting. TGA of chitosan (A) shows a weight loss in two stages. The first stage ranges between 50 and 269°C and shows about 16% loss in weight. This may correspond to the loss of adsorbed



Scheme 2

and bound water. The second stage of weight loss starts at 269°C and continues up to 330°C during which there was 37% weight loss due to the degradation of chitosan. The TGA of the grafted product (Ch-g-PAN) is different. The latter has three stages of distinct weight loss between 50 and 551°C. The first stage ranges between 50 and 92°C with 17% of the adsorbed and bound water weight loss. The second stage of weight loss starts at 92°C and continues up to 306°C, during which there was 21% weight loss due to the degradation of ungrafted Ch. There is 41% weight loss in the third stage from 306 to 659°C that contributes to the decomposition of Ch-g-PAN. At 700°C only 61% weight loss indicated a high degree of thermal stability of the graft copolymer. So, it is evident that grafting acrylonitrile onto chitosan could enhance the stability of pure chitosan. The solubility characteristic of the material is another criterion for modification, since chitosan is soluble in water in the presence of H⁺ ions (acetic acid, lactic acid, or HCl), whereas the grafted chitosans were insoluble even in solvents like DMF, which are known to solubilize PAN.

Change in the solubility behavior of the chitosan after grafting confirms the grafting. Grafted chitosan showed solubility at much higher pH than chitosan itself (graft copolymer is soluble in water at pH 5.5–6.0 while chitosan dissolves at pH 3–4), which further supported modification of the chitosan at NH₂ groups after grafting. A plausible mechanism for grafting can be proposed.

Formation of free radicals

In the presence of radical initiator

The reaction between peroxydisulfate and ascorbic acid involves chain mechanism because of the produc-

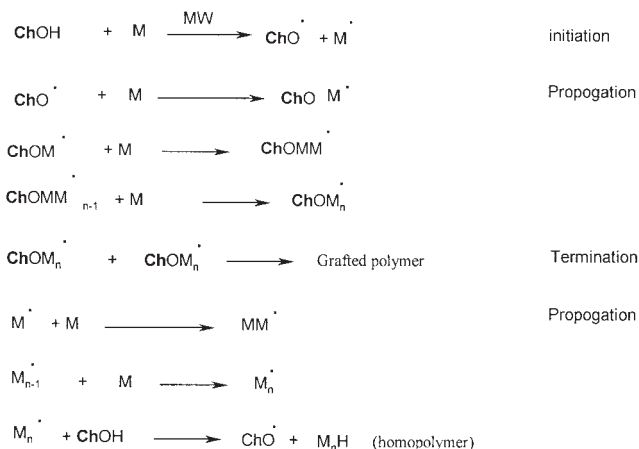
tion of sulfate ion radicals, which are well known as chain carriers (Scheme 2).

SO₄^{·-} or AH[·] may initiate graftcopolymerization by H abstraction from chitosan backbone.

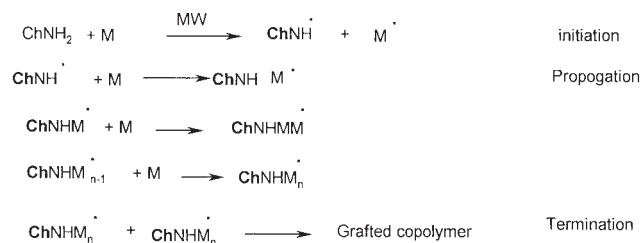
Under microwave irradiation

The chitosan molecule is quite a large molecule with pendent –OH and –NH₂ groups and these groups attached to the large chitosan molecule may behave as if they were anchored to an immobile raft and its localized rotations²⁵ therefore will be observed in the microwave region and resulting dielectric heating of the chitosan molecule may result in an enhancement of reaction rates, specifically at these groups. The dielectric heating will involve rapid energy transfer from these groups to neighboring molecules (acrylonitrile and water) because it is not possible to store the energy in a specific part of the molecule. In the chitosan molecules there are a large number of –OH groups and also –NH₂ groups and therefore this energy is expected to be enormous. This may be responsible for –OH and –NH₂ bond breaking. Further MW are also reported to have special effects²⁰ of lowering the Gibbs energy of activation of the reactions and in

Grafting at O-H groups of Chitosan



Grafting at NH₂ groups of chitosan



Where Ch stands for Chitosan
M stands for acrylamide
MW for microwave irradiation

Scheme 3

view of the above two effects a plausible free radical mechanism for the grafting under the microwave irradiation was proposed. Because the $-OH$ and $-NH_2$ groups of the chitosan are polar they will absorb MW energy and will cleave generating monomer free radical and macro radical. $O-H$ bonds are more polar than NH_2 , therefore, more grafting is expected at this site (Scheme 3).

Monomer effect

The grafting was found to increase with an increase in the initial concentration of monomer in the range of $10-28 \times 10^{-2}$ mol/L, keeping other parameters fixed. The increase in rate of grafting with the increase in acrylonitrile concentration may be due to the formation of more M_n radicals, which in turn may generate more grafting sites on chitosan by the abstraction of the H atom.

Effect of MW power and exposure time

Grafting was found to increase up to 80% MW power and thereafter decrease. More macro radicals are expected to be formed, as power is increased and grafting yield increases with MW. At $MW < 80\%$ power, yield starts decreasing, which may be due to either more homopolymerization or some decomposition of grafted copolymer taking place at MW power higher than 80%. Yield was found to increase with increase in exposure time at fixed MW power up to 1.50 min.

CONCLUSION

Chitosan-grafted-polyacrylonitrile could be efficiently synthesized without any radical initiator or catalyst in a very short reaction time of 1.5 min using MW irradiation. In the present study $K_2S_2O_8$ /ascorbic acid redox initiator was also used for the first time to synthesize the graft copolymer but grafting yield was observed more in the MW method. Thus, grafting under MW offers an economical and quick method for chitosan grafting.

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