

Microwave-Induced Rapid One-Pot Synthesis of κ -Carrageenan-*g*-PMMA Copolymer by Potassium Persulphate Initiating System

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ABSTRACT: κ -Carrageenan-*g*-PMMA copolymer has been synthesized by copolymerizing κ -carrageenan with methyl methacrylate (MMA) in aqueous medium at about pH 7. The copolymerization was carried out under microwave irradiation in the presence of a water-soluble initiator potassium persulphate. Optimum microwave irradiation conditions for obtaining maximum yields are described. The structural characteristics and thermal stability of κ -carrageenan-*g*-PMMA was studied by FTIR, NMR, and thermo gravimetric (TGA) measurements. Crystallinity of the copol-

mer was studied by powder X-ray diffraction. TGA, IR, and XRD data indicated that the κ -carrageenan was considerably modified. Optical micrograph of the copolymer was also studied. A probable mechanism of formation of the copolymer is proposed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 161–166, 2006

Key words: microwave irradiation; graft copolymer; κ -carrageenan; X-ray; modification

INTRODUCTION

The modification of the materials is important to adapt properties and hence performance to the requirements of the applications. For biogenic materials such as polysaccharides, there is a particular interest in preparation of derivatives having versatile properties, including absorbents.¹ Grafting a synthetic and natural polysaccharide is a way of creating large molecules, which have some of the properties of each polymer. Such type of works were mainly done to obtain good water absorbents and biodegradable polymers that can be cast in sheets.² Because of the large application of starch and cellulose in textile, paper, and food industry, they are being grafted or crosslinked for producing derivatives having different physicochemical properties.³

κ -Carrageenan is a seaweed-based polysaccharide and chemically consists of 3-*O*-linked D-galactopyranose and 4-*O*-linked 3,6-anhydro-D-galactopyranose (Fig. 1). A novel biopolymer-based super absorbent hydro gel synthesized through chemical crosslinking graft copolymerization of acrylic acid on to κ -carrageenan in the presence of crosslinking agent (*N,N'* methylene bisacrylamide) and an initiator (ammonium persulphate) is reported by Pourjavadi et al.⁴

Shchipunov has reported a sol-gel biomaterial based on κ -carrageenan and silica.⁵

Synthesis of alkyl glycosides and graft copolymerization of acrylic acid with starch have been efficiently carried out recently under MW irradiation.^{6,7} Microwave-promoted methylation of plant polysaccharides is reported by Singh and coworkers.⁸

In this article we report, for the first time, a microwave-induced rapid one-pot route of synthesizing very high yield graft copolymer of κ -carrageenan with methyl methacrylate in presence of potassium persulphate as initiator in aqueous medium.

EXPERIMENTAL

Materials

κ -Carrageenan used in this experiment was extracted from a red seaweed *Eucheuma cottonii* by following the method available in the literature.⁹ The products were vacuum-dried prior to reaction. Potassium persulphate (KPS), methyl methacrylate (MMA), isopropanol, and toluene used were of analytical grade and were procured from Sigma-Aldrich (Mumbai, India) and Ranbaxy Chemicals (Mumbai, India).

Apparatus

Kitchen microwave oven (LG make) having a temperature range of 40–100°C was used (Magnetrons are set at a frequency of 2450 MHz).

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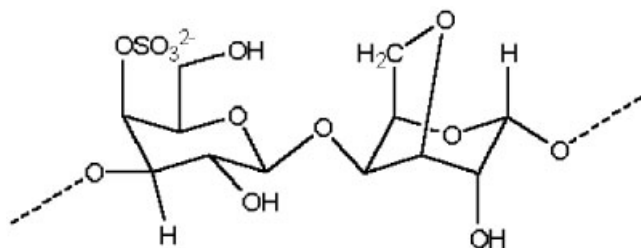


Figure 1 Repeating disaccharide units in κ -carrageenan.

Graft copolymerization and treatment of copolymer

Graft copolymerization was carried out in a 100-mL narrow-mouth conical flask. κ -carrageenan (1 g, w/v) was first dissolved in 100 mL of distilled water, followed by addition of 0.06 g (0.0022 mol/L) of KPS. MMA (2.0 g) was added to the reaction mixture and mixed well. The reaction mixture was irradiated under microwave for 120 s, with constant stirring. The reaction mixture turned milky white, which was first cooled and the product was precipitated with isopropyl alcohol (1:2.25, v/v), followed by centrifugation at 8000 rpm for 3 min. The off-white precipitate was dried and unreacted MMA was extracted from the product by Soxhlet extraction with toluene. The product was further washed with isopropyl alcohol and vacuum-dried. Unreacted MMA was recovered from the supernatant by solvent extraction with toluene. The toluene thus obtained was evaporated off and weight of unreacted MMA was determined.

Characterization

κ -Carrageenan-*g*-PMMA was characterized by FTIR analysis using a PerkinElmer Spectrum GX, FTIR System, USA, by taking 2.0 mg of sample in 600 mg of KBr. All spectra were averages of two counts with 10 scans each and a resolution of 5 cm^{-1} . The thermogravimetric analysis (TGA) of κ -carrageenan (3.32 mg) and its copolymer (3.44 mg) was carried out on a Toledo Mettler TGA system (Switzerland), a machine with a temperature program 30–600°C, at a heating rate of $10^\circ\text{C min}^{-1}$ under air atmosphere. Powder X-ray diffractions were recorded on a Philips X'pert MPD X-ray powder diffractometer using $2\theta = 10\text{--}60^\circ$. Optical microscope used was of Olympus model SZH 10 (Japan) with $70\times$ magnification.

The grafting parameters, e.g., conversion %, grafting efficiency, grafting %, were determined according to Bajpai and Rai.¹⁰

RESULTS AND DISCUSSION

Yield and grafting parameters

Yield of κ -carrageenan-*g*-PMMA was 2.86 g. Weight of unreacted MMA homopolymer was 0.12 g. Total con-

version, C% [(total weight of polymerized MMA/weight of MMA charged) \times 100], is 93%. Grafting Efficiency, E% (weight of poly-MMA grafted/total weight of poly-MMA), is $[1.86/(2-0.12)] \times 100 = 99.0\%$. Grafting percentage, G% (weight of poly-MMA grafted/weight of polysaccharide), is $[(2.86-1)/1] \times 100 = 186\%$.

Effect of the ratio of MMA to carrageenan

The influence of the ratio of MMA to agar on the graft parameters was studied and shown in Figure 2. It was found that G%, C%, and E% reached a maximum value when the ratio of MMA to κ -carrageenan was 2:1 and then decreased gradually (degradation of κ -carrageenan). Because of the limited solubility of MMA in reaction medium, the ratio of MMA to κ -carrageenan was low, resulting in lower collision probability between κ -carrageenan and MMA, leading to the low values of C%, G%, and E% (Fig. 2). It was observed that in the absence of the water-soluble initiator the reaction did not take place at all. In the presence of the initiator in the aqueous solution of κ -carrageenan, when the MMA to κ -carrageenan ratio was increased, κ -carrageenan-*g*-PMMA could play the role of self emulsifier so as to absorb more monomers (MMA) on κ -carrageenan surface, which subsequently enhanced the rate of the graft reaction, thereby sharply increasing C%, G%, and E% till the MMA to κ -carrageenan reaches 2:1. When the ratio of MMA to carrageenan was higher, chain transfer reactions were accelerated and as a result E% decreased gradually. The resulting copolymer was soluble in hot DMSO and DMF.

Effect of reaction time (duration of microwave irradiation)

The influence of the reaction time or time of microwave irradiation on grafting parameters is illustrated

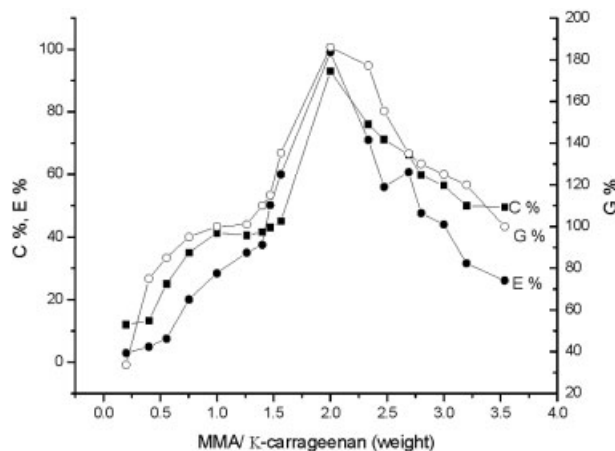


Figure 2 Effect of MMA/ κ -carrageenan ratio on grafting parameters.

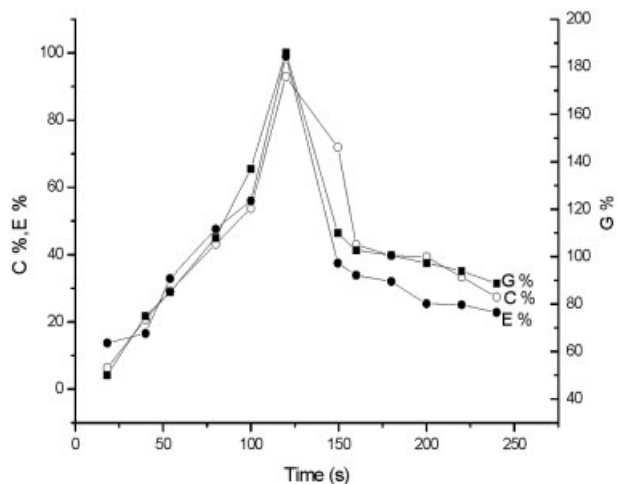


Figure 3 Effect of reaction time on grafting parameters for the formation of κ -carrageenan-g-PMMA.

in Figure 3. As expected, up to 120 s of microwave irradiation the C%, E%, and G% increased. After 120 s, these values declined gradually. This phenomenon may be explained as follows.

Microwave irradiation in presence of initiator produces hydrogen and hydroxyl free radicals by vibrating water. Simultaneously, it produces alkoxy radicals on κ -carrageenan. The sulfate free radicals generated from KPS absorbed the hydrogen radical (produced by vibrating water and κ -carrageenan molecules), resulting in the formation of sulfuric acid. The hydroxyl radical produced (by vibrating water molecule) formed KOH by reacting with potassium radical. At lesser duration of microwave exposure, there was a balance in formation of sulfuric acid and KOH, leading to neutral pH of the reaction medium, which was actually observed. But as the duration of microwave exposure increased, the balance of sulfuric acid and KOH tripped toward acidic pH, which was actually observed, leading to the degradation of the product.

Effect of temperature

When the other reaction conditions were constant (MW time, 120 s; MMA/ κ -carrageenan, 2:1), the grafting parameters at various temperatures are shown in Figure 4. In accordance with the general rule of radical polymerization, E% increases and then levels off. In this type of microwave-induced reactions, with increasing temperature, the vibration of reactant molecules as well as the reaction medium increases; as a result, the activation energy required to form the product decreases, increasing the reaction rate. But after a certain temperature the vibration of the molecules reaches the optimum condition and reaction rate levels off. Again when temperature increases the excessive vibration leads to destruction of polymer

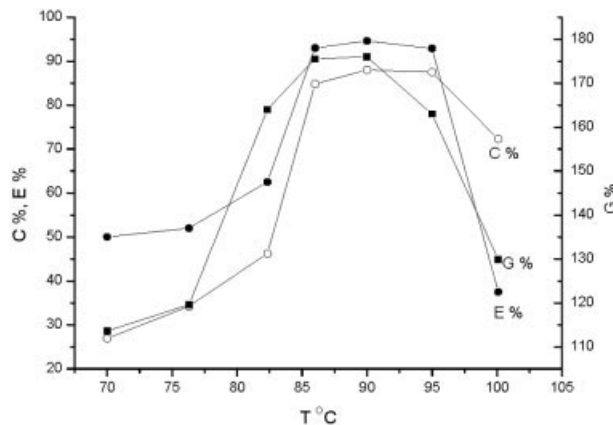


Figure 4 Effect of reaction temperature on grafting parameters for the formation of κ -carrageenan-g-PMMA.

chains and as a result products with lower C%, E%, and G% values are obtained. In this type of reaction there is no product formation in the reactions carried out at temperatures less than 70°C.

Effect of initiator concentration of grafting parameters

KPS was added in the range of 0.009–0.14 g in the reaction mixture. It was observed that, initially, when initiator concentration was low the C%, E%, and G% values were also low. This may be because small amount of initiator is not sufficient to fully cleave the bond between O and H in the polysaccharide (at C-6) under microwave irradiation conditions. The values gradually increased up to 0.06 g (0.0022 mol/L) of initiator concentration and then leveled off to 0.09 g (0.0033 mol/L), but beyond this, because of excess initiator concentration there was cleavage of more bonds (at C-2, C-4) and as a result the values declined (Fig. 5).

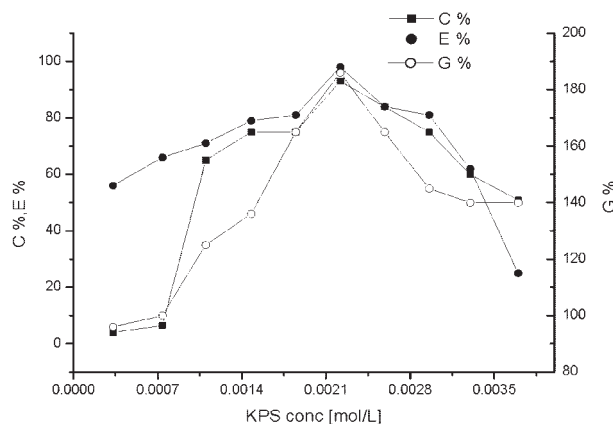


Figure 5 Optimization of quantity of initiator in the formation of κ -carrageenan-g-PMMA.

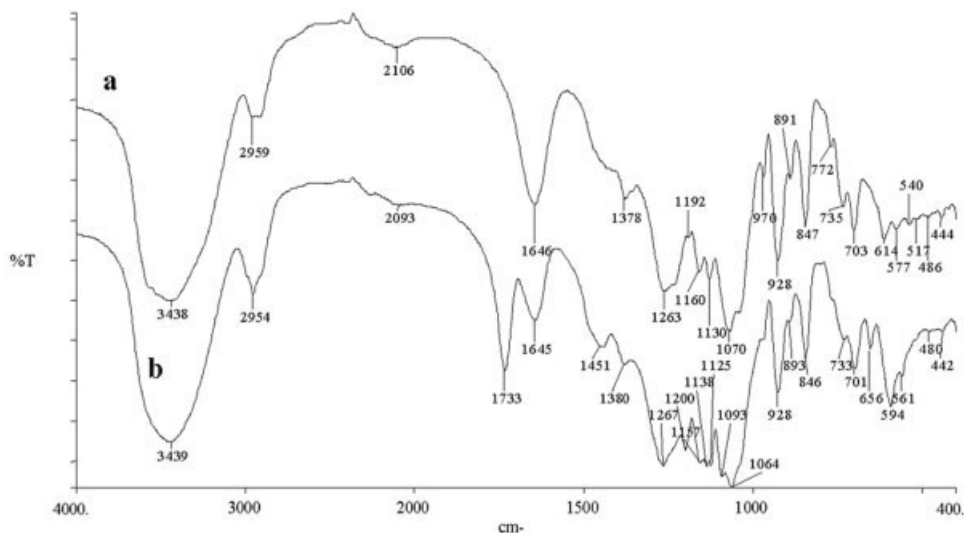


Figure 6 FTIR spectra for (a) control κ -carrageenan and (b) κ -carrageenan-g-PMMA.

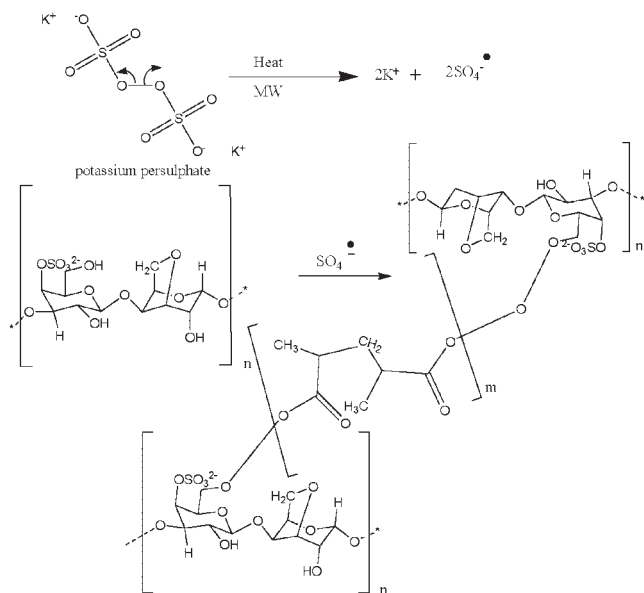
IR spectral studies

The grafting was confirmed by comparing the IR spectrum of κ -carrageenan with that of the grafted product and the results obtained are shown in Figure 6. The main difference observed is the appearance of a carbonyl absorption band at 1733 cm^{-1} for κ -carrageenan-g-MMA copolymer. Appearance of a carbonyl absorption band at 1733 cm^{-1} for the copolymer indicated insertion of the MMA unit on κ -carrageenan. Characteristic IR bands at 740 , 773 , and 930 cm^{-1} due to 3,6-anhydro- β -galactose skeletal bending of κ -carrageenan^{11,12} in the copolymer indicated that during grafting κ -carrageenan was not decomposed. Presence

of band at 844 cm^{-1} , which is due to C-4 sulfate of carrageenan, indicates that the free radical formation took place on OH group of κ -carrageenan (C-6 carbon) rather than on the sulfate moiety (Scheme 1).

Thermal analysis

Thermo gravimetric analysis (TGA) of κ -carrageenan and the grafted copolymer is shown in Figure 7. In case of κ -carrageenan copolymer there are two stages of mass loss. First stage was from 30 to 280°C . The initial weight loss (ca. 5%) may be due to bound water in κ -carrageenan. Again there was a 10–20% mass loss between 240 and 280°C ; this may be due to degradation of the κ -carrageenan product. In the next step, about 40–50% mass loss was observed in temperature range of 320 – 410°C . But for the graft copolymer the



Scheme 1 Proposed mechanism for formation of κ -carrageenan-g-PMMA copolymer.

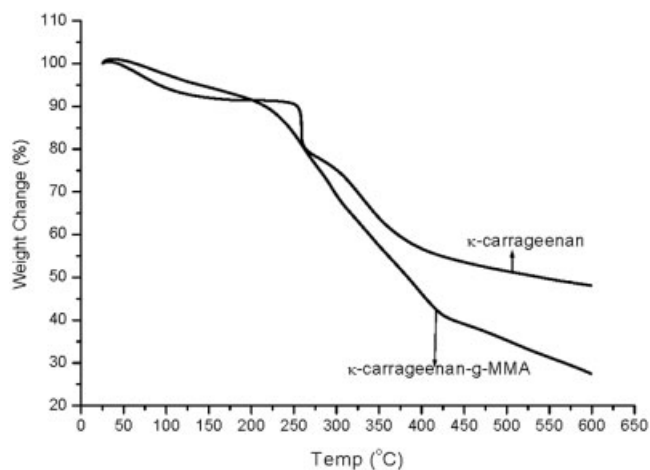


Figure 7 Thermogravimetric (TGA) profile for pure κ -carrageenan and κ -carrageenan-g-PMMA copolymer.

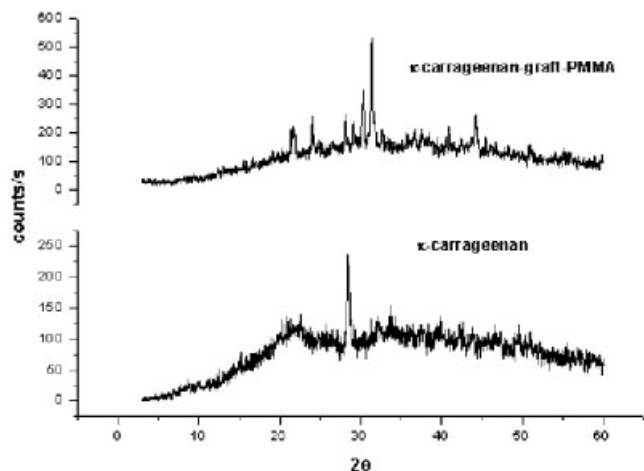


Figure 8 X-ray diffraction of pure κ -carrageenan and κ -carrageenan-g-PMMA copolymer.

mass loss took place only in one stage. About 60% mass loss took place at temperature ranges between 250 and 500°C. It is evident that grafting of MMA on κ -carrageenan has modified the thermal property of κ -carrageenan.

X-ray diffraction analysis

The X-ray diffraction spectra of pure κ -carrageenan and its copolymer were measured as shown in Figure 8. It was observed from the X-ray diffraction spectrum of native κ -carrageenan that it has one sharp peak ($2\theta = 29.1^\circ$); after grafting with MMA the copolymer shows three sharp peaks ($2\theta = 27.2^\circ, 29.1^\circ$, and 31.2°). This result manifested that along with amorphous part the crystalline part of κ -carrageenan also took part in grafting. The crystallinity indices were determined using the methods described by Herman and Weidinger.¹³ The crystallinity index for native κ -carrageenan was found to be 0.0847 and for graft copolymer 0.2536; that is, crystallinity was increased by 3 times in the graft copolymer of carrageenan.

Morphology

Optical micrographs of the copolymer were taken with 70 \times magnification and compared with those of κ -carrageenan (Fig. 9). Scrutiny of these figures revealed that the morphology of κ -carrageenan was modified.

Proposed mechanism of copolymerization

Crosslinking and graft copolymerization of poly-MMA onto the backbone of κ -carrageenan was carried out in an aqueous medium using KPS as free radical initiator and MMA as the crosslinking agent. The proposed mechanism for this graft copolymerization is illustrated in Scheme 1. Presumably, the sulfate anion radical produced from thermal decomposition of KPS abstracts hydrogen from the hydroxy group of κ -carrageenan to form corresponding alkoxy radicals on the substrate (C-6 carbon atom of κ -carrageenan). Further, this anion radical also initiates polymerization of MMA to afford poly methylmethacrylate (PMMA) radicals. Then the resulting κ -carrageenan macro radicals initiate graft copolymerization with PMMA. It would be reasonable to assume that PMMA radicals would also be involved in crosslinking (cf. 4). Further studies, however, are needed to understand the actual mechanism.

CONCLUSIONS

The feasibility of grafting on natural seaweed-based polysaccharides such as κ -carrageenan by microwave irradiation has been demonstrated. The most important advantage of this method is that the reaction conditions are very simple and duration of reaction is short. Many chemical reactions lead to degradation of these types of polysaccharides because of their very high acid sensitivity, but in this reaction it has been shown that microwave irradiation under controlled conditions can result in the formation of undegraded

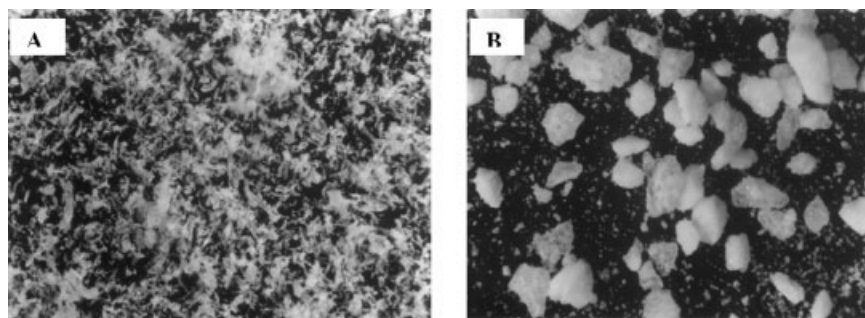


Figure 9 Optical micrographs of (A) control κ -carrageenan and (B) κ -carrageenan-g-MMA.

copolymer of κ -carrageenan. This work may help popularize microwave irradiation technique for graft copolymerization reactions.

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