

Ceric-induced grafting of acrylonitrile onto sodium salt of partially carboxymethylated guar gum

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Abstract

The optimum reaction conditions for affording maximum percentage of grafting have been established in the case of grafting of acrylonitrile (AN) onto Na-PCMGG ($\overline{DS} = 0.497$) using ceric ammonium nitrate (CAN) as a redox initiator, in an aqueous medium, by successively varying reaction conditions such as concentrations of nitric acid, ceric ammonium nitrate, monomer (AN) as well as reaction time, temperature and amount of substrate. The influence of these reaction conditions on the grafting yields have been discussed. The overall activation energy of grafting has been calculated. The IR-spectroscopic, thermal (TGA/DSC) and scanning electron microscopic (SEM) techniques have been used for the characterization of the graft copolymer.

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1. Introduction

Considerable interests have been shown on the chemical modification of natural macromolecules for imparting desirable properties onto them. In recent years, chemical modification of natural polymers through grafting has received considerable attention and has made paramount contribution towards better industrial and biomedical applications. In previous papers, we reported ceric-induced (Shah, Patel, & Trivedi, 1992, 1993) and Fenton's reagent initiated (Shah, Patel, & Trivedi, 1994a,b) grafting of acrylonitrile onto sodium alginate (SA) and investigated the biodegradable behaviour of SA graft acrylonitrile by studying its interactions with various microorganisms (Shah, Ramesh, Patel, & Trivedi, 1994c). We have also grafted ethyl acrylate (Shah, Patel, & Trivedi, 1994d), methyl acrylate (MA) and methyl methacrylate (MMA) (Shah, Patel, & Trivedi, 1995) onto SA in the presence of Ce^{+4} and studied the thermal behaviour of the graft

copolymers (Shah, Patel, & Trivedi, 1996). We have also reported ceric-induced grafting of methyl acrylate onto sodium salt of partially carboxymethylated sodium alginate (Patel, Patel, & Trivedi, 1999) and synthesis, characterization and evaluation of sodium salt of partially carboxymethylated starch graft poly(methyl methacrylate) copolymers as a New Biodegradable Plastics (Rex, Datta, & Trivedi, 2002) as well as the evaluation of the graft copolymers of Agar for sustained release of Diclofenac sodium from tablet (Umatt, Patel, & Trivedi, 2001).

In the present investigation we have modified Guar Gum (GG), a naturally occurring plant-derived polysaccharide of great commercial importance, by carboxymethylation, as the derivatization enhances the behaviour of GG toward grafting due to the combined influence of the following factors: (a) carboxymethyl groups increase the swellability of GG, thereby facilitating diffusion of the monomer and initiator, and (b) the ionization of carboxyl groups along the guar gum chains introduces negative charges which attract ceric ions to the GG molecules leading to the formation of more active sites, available for the monomer, thus increasing the reactivity of GG.

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Literature survey reveals that recently a good amount of work on grafting of various vinyl monomers onto guar gum using different initiating systems has been carried out (Chowdhary, Samui, Kundu, & Nandi, 2001; Kamel, El-Thalouth, & Abd, 2000; Kunj, Taunk, & Tripathi, 1999; Kunj, Taunk, Tripathi, & Kumar, 2000; Kunj, Kumar, Tripathi, & Pandey, 2001; Taunk, 2000). However, the data on the grafting of vinyl monomers onto sodium salt of partially carboxymethylated guar gum are scanty. As a part of our research programme, we have therefore successfully carried out the modification of sodium salt of partially carboxymethylated guar gum (Na-PCMGG, $\overline{DS} = 0.497$) by graft copolymerization with methyl acrylate (MA) (Trivedi, Kiran, Patel, & Trivedi, 2004a), methyl methacrylate (MMA) (Trivedi, Kiran, Patel, & Trivedi, 2004b), ethyl methacrylate (EMA) (Trivedi, Kiran, Patel, & Trivedi, 2004c) using ceric ammonium nitrate (CAN) as a redox initiator as well as using CAN as a Photoinitiator (Thaker & Trivedi et al., 2004 a,b). Recently, we have also compared the reactivity of different vinyl monomers towards grafting (Trivedi, Kiran, Patel, & Trivedi, 2004d) and studied the effects of substrate structure and liquor ratio on percent grafting (Trivedi, Kiran, Patel, & Trivedi, 2004e) using the optimum reaction conditions established for affording maximum percentage of grafting of different vinyl monomers onto Na-PCMGG ($\overline{DS} = 0.497$).

This paper presents the results of the evaluation of the optimized reaction conditions of grafting of acrylonitrile onto the sodium salt of partially carboxymethylated guar gum (Na-PCMGG) by using the tetravalent cerium ion as well as the characterization of the graft copolymer by using different techniques. The studies on the potential application of the graft copolymer (Na-PCMGG-g-PAN) as super absorbent is in progress and the results will be published elsewhere.

2. Experimental

2.1. Materials

Guar gum (GG) was kindly supplied by H.B. Gum Industries Pvt. Ltd; Kalol (Gujarat/India). The method of preparation and purification, as well as the measurement of degree of substitution (\overline{DS}) of the sodium salt of partially carboxymethylated guar gum (Na-PCMGG) were followed as described earlier (Joshi, Sinha, Patel, & Trivedi, 1995; Trivedi, Patel, & Patel, 1978). The \overline{DS} of Na-PCMGG was found to be 0.497. AN (Samir Tech. Chem.) was distilled out at atmospheric pressure and the middle fraction was collected and used. CAN of reagent grade (Chiti Chem; Baroda) was used as received. Analar grade nitric acid was used. Fresh solutions of the initiator were used, made by dissolving the required amount of CAN in nitric acid. All other reagents and solvents used in the present work were of reagent grade. N_2 gas was purified by passing through fresh

pyrogallol solution. Deionized water was used for the preparation of solutions as well as for polymerization reactions.

2.2. Graft copolymerization

A 500 ml three-necked flask equipped with mechanical stirrer, a reflux condenser and a glass inlet system was immersed in constant temperature bath for grafting reactions. In a typical reaction, varying amount (0.5×10^{-3} – 3.0×10^{-3} kg, dry basis) of Na-PCMGG ($\overline{DS} = 0.497$) was dissolved in low conductivity water (100 ml) with constant stirring and bubbling a slow stream of nitrogen for 1 h at the desired temperature (20–45 °C). Freshly prepared 10 ml solution of CAN (2.5×10^{-3} – 8.0×10^{-2} M) in nitric acid (nil to 1.0 M) was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction solution and freshly distilled AN (0.037–0.370 M) was added. The grafting reactions were carried out for varying time intervals (0.5–10 h). After completion of the reaction, the mixture was immediately poured into excess of methanol to precipitate out the polymer. The crude copolymer product was filtered, repeatedly washed with nitric acid as well as 90% methanol and finally washed with pure methanol. The crude copolymer thus obtained was dried under vacuum at 40 °C. The homopolymer poly (acrylonitrile) (PAN) was separated from the crude graft copolymer by extraction with dimethyl formamide for 48 h. After complete removal of the homopolymer, the pure graft copolymer was dried at 40 °C under vacuum to a constant weight.

The percentage of grafting (%G), percentage of grafting efficiency (%GE) as well as rates of polymerization (R_p), graft copolymerization (R_g) and homopolymerization (R_h) were evaluated by using expressions as mentioned earlier (Vijaykumar, Reddy, & Joseph, 1985).

2.3. IR spectra

IR spectra of Guar Gum, Na-PCMGG ($\overline{DS} = 0.497$), Na-PCMGG-g-PAN and PAN were taken in KBr pellets using Nicolet impact 400D Fourier Transform Infra Red Spectrophotometer.

2.4. Thermogravimetric analysis (TGA)

The thermal behaviour of Guar Gum, Na-PCMGG ($\overline{DS} = 0.497$), Na-PCMGG-g-PAN and PAN has been examined in an inert atmosphere at a heating rate of 10 °C/min with the help of the Dupont 951 thermogravimetric analyzer.

2.5. Differential scanning calorimetry (DSC)

The DSC scans of Guar Gum, Na-PCMGG ($\overline{DS} = 0.497$), Na-PCMGG-g-PAN and PAN have been

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