Modified CMC. 4. Ceric-initiated Methacrylonitrile Graft Polymerization onto Carboxymethylcellulose

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 ABSTRACT

Graft copolymerization of methacrylonitrile (MAN) onto carboxymethylcellulose (CMC) was carried out under argon atmosphere in a homogeneous aqueous medium by using ceric ammonium nitrate (CAN) as an initiator. The FTIR spectroscopy and solubility characteristics of the products were used for confirming the graft copolymer formation. The effect of the concentration of the initiator, monomer and polysaccharide as well as the reaction time and temperature on the graft copolymerization reactions were investigated to achieve the optimum grafting conditions (i.e. CAN 0.00065 mol/L, MAN 0.85 mol/L, CMC 1% W/V, reaction temperature 45°C, and reaction time 2 h). According to the empirical rates of the polymerization and the graft copolymerization of MAN onto CMC backbone, the overall activation energy of the graft copolymerization reaction was estimated to be 29.8 kJ/mol.

KEY WORDS: Carboxymethyl cellulose, methacrylonitrile, ceric ammonium nitrate, graft copolymerization.

INTRODUCTION

During the past decades, considerable research was being carried out on the graft copolymerization of hydrophilic and hydrophobic vinyl monomers onto polysaccharides1-5. These biodegradable and low cost graft copolymers, with new properties, can be used in many applications such as textiles, paper industry, agriculture, medical treatment and also in petroleum industry as flocculants and thickening agents1-3,6-9. Free radical graft copolymerization was usually carried out by using various initiators such as ammonium persulfate, benzoyl peroxide and azoisobutyronitrile. Mino and Kaizerman for the first time utilized ceric ammonium nitrate (CAN) as a very effective redox initiator10. CAN is an efficient oxidizing agent that can create free radicals capable of initiating graft copolymerization of vinyl monomers onto polysaccharides. For example, methyl acrylate was grafted onto starch using Ce (IV) as an initiator11,12. Ceric ions have been also used to graft copolymerized some vinyl monomers including acrylonitrile13, methyl acrylate and methyl methacrylate14, and acrylamide15,16 onto sodium alginate. In addition, ceric ion was recently used to graft copolymerization of acrylamide onto carboxymethyl starch17 and carboxymethylcellulose18. Starch-g-poly (methacrylonitrile)19 and cyanoethylcellulose-g-poly(acrylonitrile)20 was also prepared by this method. There have been many investigations dealing with the grafting of various monomers
onto the most well-known water-soluble cellulose derivative, i.e., carboxymethylcellulose. But a literature survey reveals that no paper has been reported in the case of methacrylonitrile (MAN) grafting onto this industrial polysaccharide. Therefore, in the present work, we attempted to modify CMC by free radical graft copolymerization of methacrylonitrile. The grafting reaction was carried out in an aqueous solution by CAN as a redox initiator in dilute nitric acid solution. The effect of concentration of CMC, MAN and CAN as well as the reaction time and temperature on the graft copolymerization was studied by determining the grafting parameters.

**EXPERIMENTAL**

**Materials**

A commercial grade carboxymethylcellulose (degree of substitution 0.52) was used in this work. Ceric ammonium nitrate was purchased from Merck and was used without purification. It was employed as a freshly 0.1 mol/L acidic solution (2.74 g CAN in 50 mL of 1 N nitric acid), unless in the case of the initiator series of experiments. Methacrylonitrile (from Merck) was used after distillation for removing of inhibitor. All other chemicals were of analytical grade.

**Graft Copolymerization Procedure**

A weighed amount of CMC was dissolved in 50 mL of distilled water in a 100 mL two-necked flask equipped with magnetic stirrer, immersed into a thermostated water bath, preset at 45°C. An inert gas (argon) was gently bubbled into the reactor to remove the oxygen during the graft copolymerization reaction. After 15 min, various amounts of MAN monomer were added to the reaction mixture at once, and the mixture was allowed to stir for 10 min. Then a given volume of freshly prepared solution of CAN was added and the graft copolymerization reaction was conducted for 2 h. Finally, the resulted product was precipitated by pouring the reaction mixture into 250 mL of methanol, and the precipitate was filtered and repeatedly washed with methanol.

**Homopolymer Extraction**

The graft copolymer, namely CMC-g-PMAN, was freed from polymethacrylonitrile (PMAN) homopolymer, by pouring 0.50 g of the product in 50 mL of dimethylformamide solution. The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer, the CMC-g-PMAN was filtered, washed with methanol and dried in an oven at 50°C to reach a constant weight.

**Infrared Spectroscopy**

FTIR spectra of grafted and ungrafted CMC were run in the form of KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer.

**RESULTS AND DISCUSSION**

**Evidence of Grafting**

**Solubility Test**

The simplest method to prove the formation of CMC-g-PMAN is based on the solubility difference of the graft copolymer and the non-grafted homopolymer. CMC and PMAN are soluble in water and DMF, respectively. When a reaction product was extracted with DMF and alternatively with water for 24 h, an insoluble solid still remained. A physical mixture of CMC and PMAN was treated in the same way and was found to dissolve completely. Therefore, it is obvious that the resulted graft copolymer was not a simple physical mixture, but some chemical bonds must exist between the CMC substrate and PMAN macromolecules.

**Infrared Spectroscopy**

The existence of PMAN grafting was also confirmed by the difference between FTIR spectra of the grafted and non-grafted products (Fig. 1). An additional sharp characteristic peak in the graft copolymer at 2244 cm\(^{-1}\) (Fig. 1b) which is attributed to –CN stretching absorption can be used for confirming the grafting of PMAN onto the substrate, CMC.

**Synthesis, Mechanism and Reaction Rate**

Duke and coworkers\(^{21,22}\) have shown that ceric salts form complexes with alcohols, and these complexes are disproportionate via single electron transfer with the formation of free radicals.
on the reducing agent. On the other hand, it has been shown that the anhydroglucose units are predominantly oxidized through C$_2$–C$_3$ bond cleavage induced by Ce (IV) ions$^{23}$. Therefore, a general reaction mechanism for graft copolymerization reaction, in analogy with that previously mentioned$^{24}$ may be as follows (Scheme 1): the first step of the mechanism is a complex formation of the Ce$^{4+}$ ion with the oxygen atom at the C-2 position and the hydroxyl group at the C-3 position. This CMC-Ce$^{4+}$ complex are then reduced to a Ce$^{3+}$ ion and consequently a free radical is formed onto CMC backbone. These radicals are responsible for the initiation of methacrylonitrile grafting onto polysaccharide backbone.

The rates of polymerization ($R_p$) and graft copolymerization ($R_g$) may be evaluated as measures of the rate of monomer disappearance by using the following equation$^{25}$.

$$R_p \quad \text{(mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3}) = \frac{\text{Weight of total polymer formed}}{\text{Molecular weight of monomer} \times \left[\text{reaction time (s)} \times \text{volume (m}^3)\right]} \quad (1)$$

$$R_g \quad \text{(mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3}) = \frac{\text{Weight of grafted polymer}}{\text{Molecular weight of monomer} \times \left[\text{reaction time (s)} \times \text{volume (m}^3)\right]} \quad (2)$$

The calculation of $R_p$ values may be of significant importance in confirming a proposed reaction mechanism and kinetics. Therefore, we investigated the relation between rate of graft copolymerization and concentration of CAN, MAN and CMC. Figures 2-4 show that the plots of $R_p$ versus the monomer concentration, $[\text{MAN}]$, half-order of the initiator concentration, $[\text{Ce}^{4+}]^{1/2}$ and the polysaccharide concentration, $[\text{CMC}]^{1/2}$, are linear. This is in agreement with a
modified kinetic scheme recently explored for CAN-initiated methyl acrylate grafting onto sago starch. The statement of rate of polymerization according to the scheme is as follows:

\[ R_p = k_p \left( K \frac{k_d}{k_p} \right)^{1/2} \left[ CMC \right]^{1/2} \left[ Ce^{4+} \right]^{1/2} \left[ MAN \right] \]

(3)

The coefficient \( K \) is the equilibrium constant, \( k_p \), \( k_d \), and \( k_t \) are the rate constants for propagation, CMC-meric complex dissociation, and termination reactions, respectively. Therefore, we preliminarily conclude that the CAN-initiated
Characteristic Grafting Parameters

The percentage of grafting ratio (%Gr), grafting efficiency (%Ge), add-on (%Ad) and homopolymer (%Hp) were evaluated with the following weight basis expressions as reported by Fanta:

\[
%Gr = \frac{\text{PMAN grafted}}{\text{Initial CMC}} \times 100 \quad (4)
\]

\[
% Ge = \frac{\text{PMAN grafted}}{\text{Monomer charged}} \times 100 \quad (5)
\]

\[
% Ad = \frac{\text{PMAN grafted}}{\text{Graft copolymer}} \times 100 \quad (6)
\]

\[
% Hp = (1 - Ge) \times 100 \quad (7)
\]

%Gr is the weight percent of the graft copolymer synthetic part (PMAN grafted) formed from initial CMC used. %Ge stands for the grafted PMAN formed from initial monomer charged. %Ad is the weight percent of the grafted PMAN of the graft copolymer CMC-g-PMAN. %Hp denotes the weight percent of the homopolymer graft copolymer formed from initial monomer charged.

Optimization of the Reaction Conditions

In the present investigation, the effect of concentration of CMC, CAN and MAN, along with reaction time and temperature was studied, to optimize the reaction conditions. It may be found from the related curves (next figures) that the trends of the “changes” are similar for grafting parameters Gr, Ge, and Ad. The reason is the similar concepts applied for defining the grafting parameters (Eqs. 4-6).

Effect of Initiator Concentration

The effect of concentration of CAN on graft polymerization was studied by changing its concentration from 0.0003 to 0.0008 mol/L (Fig. 6). It was observed that with increasing CAN concentration, from 0.0003 to 0.00065 mol/L, both
%Gr and %Ge were increased. Further increase of concentration of CAN beyond 0.00065 mol/L disfavored the grafting parameters. The initial increase in %Gr and %Ge may be attributed to increased number of active free radical sites on the CMC backbone. The decrease of grafting parameters at higher concentration of CAN may be due to (a) oxidative degradation of CMC chains by excess Ce⁴⁺ ions, (b) an increase in the termination reaction of the chain radicals via bimolecular collision because of an increased population of macroradicals produced, and (c) enhancement in homopolymerization reaction. These observations are in agreement with similar observations reported by others²⁸,²⁹.

**Effect of Monomer Concentration**

Figure 7 shows the influence of monomer concentration on grafting parameters. These parameters were found to be increased by enhancement of methacrylonitrile concentration from 0.48 up to 1.32 mol/L. This behavior can be attributed to the increase of monomer concentration in the vicinity of the CMC backbone and consequent greater availability and enhancement chances for molecular collisions of the reactants. The decrease of %Gr and %Ge with further increase in the MAN concentration may be explained as follows: (a) preferential homopolymerization over graft copolymerization, (b) increasing the viscosity of reaction medium, which hinders the movement of free radicals, and (c) increase in the chance of chain transfer to monomer molecules. Similar observations have been reported for the grafting of ethyl acrylate onto cellulose³⁰, methyl acrylate onto starch³¹, and methyl methacrylate onto sodium alginate¹⁴.

**Effect of CMC Concentration**

The effect of CMC concentration on graft copolymerization was depicted in Fig. 8. With increasing the CMC amount, more reactive grafting sites are formed which is favorable for grafting. This can account for initial increment in grafting parameters up to 1.0% W/V of CMC value. Beyond this amount, the grafting values were diminished. This may be ascribed to the increase in viscosity of reaction mixture and the termination reaction between macroradical-macroradical and macroradical-primary radicals as well. This observation is in close agreement with the results obtained by other investigators³²-³⁴.

**Effect of Reaction Temperature**

Figure 9 shows the effect of temperature on the grafting parameters. The increase in tempera-
may be attributed to the substantial increase in the rate of chain transfer and chain termination reactions between grafted chains and monomer molecules. Similar behavior was observed in the case of grafting of acrylic acid onto methyl cellulose\cite{35} and acrylamide onto xanthan gum\cite{36}.

**Effect of Reaction Time**

Figure 10 presents the relationship between the reaction time and the grafting parameters. The maximum percentage of grafting (%Gr) was observed at 2 h, and thereafter it gradually decreased. It is obvious that the longer the reaction time, the better the graft copolymerization yield. The grafting loss may be attributed to decrease of all the consuming reactants. In addition, the decreased number of available active free radical sites for grafting and the retardation of diffusion of reactants, because of the long grafted chains at the CMC surface, may be other possible reasons for the diminished grafting at longer reaction times. Similar time dependency of grafting parameters was reported by others\cite{37,38}.


ture from 35 to 45 ±1°C favors the activation of macroradicals and monomeric radicals, i.e. with increase of the temperature up to 45°C, the kinetic energy of reactants is increased and the rate of polymerization is enhanced. In addition, high temperature increases the solubility of the monomer in the reaction mixture and favors the monomer diffusion into the CMC substrate and therefore, leads to an increase in grafting parameters was observed. Temperatures higher than 45°C disfavor the grafting parameters. This.
physical significance of the grafting parameters is more influenced by the initial substrate rather than the initial monomer charged. So, each reaction variable influences on Gr much more than on Ge. In other words, the parameter Gr is more sensitive to the initial reactants than Ge.

CONCLUSION

Novel graft copolymers were synthesized by grafting of methacrylonitrile onto carboxymethylcellulose in the presence of cerium (IV) ammonium nitrate as an efficient initiator in acidified aqueous medium, under inert atmosphere. The main factors affecting the grafting parameters, including concentration of the initiator monomer and polysaccharide, reaction time and temperature was studied in detail. The optimum reaction conditions were found to be CAN 0.00065 mol/L, MAN 0.96 mol/L, CMC 1% W/V, reaction temperature 45°C and reaction time 2 h. Under the optimized conditions the grafting parameters were calculated to be Gr 115%, Ge 97%, Ad 75%, and Hp 3%. Empirical polymerization rate showed a first-order dependence on the monomer concentration and a half-order dependence on the initiator concentration. According to the slope of ln Rg versus l/T, the overall activation energy for graft copolymerization reaction was estimated to be 29.8 kJ/mol. As an extension of this work, the CMC-g-PMAN copolymer is being subjected to further modification to prepare thickeners and flocculants for aqueous systems.

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