



Rate Evaluation of the Graft Polymerization of Buthylmethacrylate and Acrylic acid onto Carboxymethylcellulose

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ABSTRACT

Graft copolymerization of Buthylmethacrylate (BMC) and Acrylic acid (AcA) onto carboxymethylcellulose (CMC) was carried out under argon atmosphere in a homogeneous aqueous medium by using ceric ammonium nitrate (CAN) as an initiator. A plausible reaction mechanism of grafting has been suggested. According to the empirical rates of the polymerization and the graft copolymerization of BMC and AcA onto CMC backbone, the overall activation energy of the graft copolymerization reaction was estimated to be 29.8 kJ/mol.

Key words: Carboxymethylcellulose, Buthylmethacrylate, Acrylic acid, Graft copolymerization.

INTRODUCTION

During the past decades, considerable research was being carried out on the graft copolymerization of hydrophilic and hydrophobic vinyl monomers onto polysaccharides. 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 agents¹⁻⁴. 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

initiator⁵. 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 initiator. Ceric ions have been also used to graft copolymerized some vinyl monomers including acrylonitrile, methyl acrylate and methyl methacrylate, and acrylamide onto sodium alginate. In addition, ceric ion was recently used to graft copolymerization of acrylamide onto carboxymethyl starch and carboxymethylcellulose¹⁸. Starch-g-poly(methacrylonitrile) and cyanoethylcellulose-g-poly(acrylonitrile) 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 Graft Polymerization Simultaneously of Buthylmethacrylate and Acrylic acid Monomers onto Carboxymethylcellulose. Therefore, in the present work, we attempted to evaluation of rate CMC by free radical graft copolymerization of Buthylmethacrylate and Acrylic acid Monomers. The grafting reaction was carried out in an aqueous solution by CAN as a redox initiator in dilute nitric acid solution⁶⁻⁷.

EXPERIMENTAL

Materials

The polysaccharide, Carboxymethylcellulose (CMC, degree of substitution 0.52, from Condinson Co., Denmark) was of analytical grade and was used as received. 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. The monomers, Acrylic acid (AcA, from Merck) and Buthylmethacrylate (BMC, from Merck) were used after distillation for removing 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 55°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 BMC and AcA monomer were added to the reaction mixture at once. 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 solution into 250 mL of methanol, and the precipitate was filtered and repeatedly washed with methanol⁸⁻¹¹.

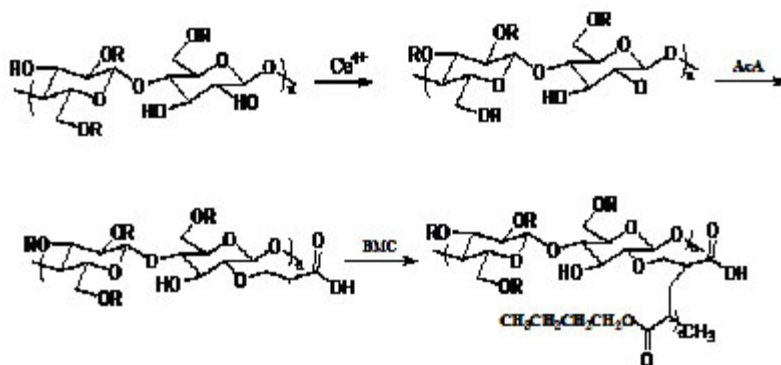
Homopolymer extraction

The graft copolymer, namely CMC-g-PAcA-co-PBMC, was freed from poly acrylic acid and poly Buthylmetacrylate homopolymers, by pouring 0.50 g of the product in 50 mL of ethanol solution. The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymers, the CMC-g-PAcA-co-PBMC was filtered, washed with methanol and dried in oven at 50°C to reach a constant weight¹².

RESULTS AND DISCUSSION

Synthesis, mechanism and reaction rate

Duke and coworkers 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 (CMC macroradicals). The mixture monomers, which are in vicinity of the macroradical sites, become acceptor of CMC radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighboring molecules leading to propagation. These grafted chains are terminated by coupling to give the graft copolymer.



Scheme 1: General reaction mechanism for graft copolymerization of AcA and BMC onto CMC backbone in the presence of ceric (IV) ion

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 Simultaneously of Butylmethacrylate and Acrylic acid grafting onto polysaccharide backbone¹³⁻¹⁴.

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 equations:

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

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

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

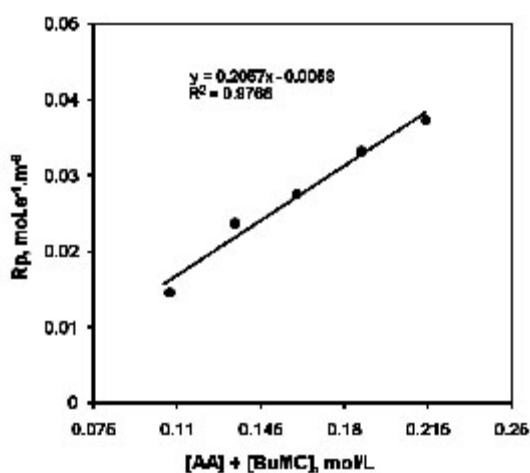


Fig. 1: Plot of R_p versus monomers (AcA-BMC) concentration

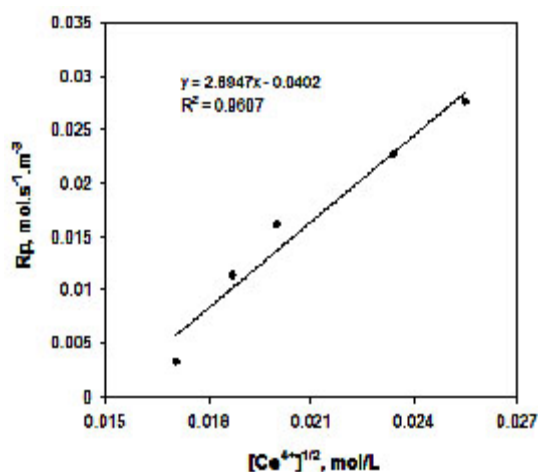


Fig. 2: Plot of R_p versus $[Ce^{4+}]^{1/2}$

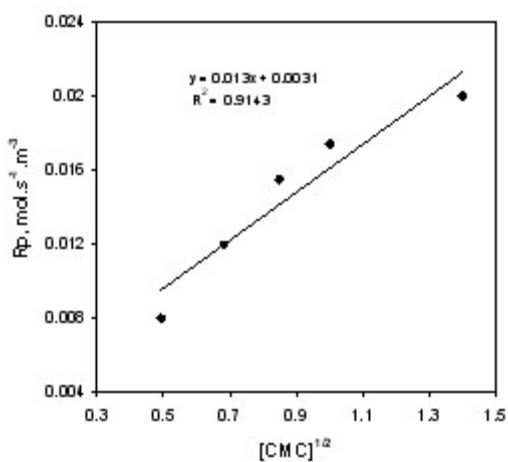


Fig. 3: Plot of R_p versus $[CMC]^{1/2}$

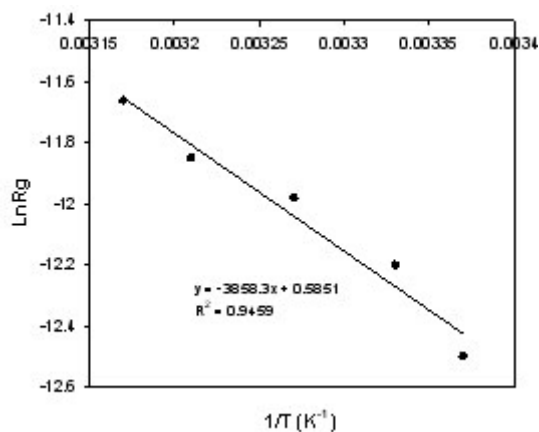


Fig. 4: Plot of $\ln R_g$ versus $1/T$ for estimating the activation energy of the graft polymerization reaction

copolymerization and concentration of CAN, AcA-BMC and CMC. Figures 1-3 show that the plots of R_p versus the monomers concentration, $[AcA] + [BMC]$, half-order of the initiator concentration, $[Ce^{+4}]^{1/2}$ and the polysaccharide concentration, $[CMC]^{1/2}$, are linear(15). This is in agreement with a modified kinetic scheme recently explored for CAN-initiated methacrylate grafting onto sago starch²⁶. The statement of rate of polymerization according to the scheme is as follows:

$$R_p = k_p (K k_d / k_t)^{1/2} [CMC]^{1/2} [Ce^{+4}]^{1/2} [AcA] [BMC] \quad \dots(3)$$

The coefficient K is the equilibrium constant, k_p , k_d and k_t are the rate constants for propagation, CMC–ceric complex dissociation, and termination reactions, respectively. Therefore, we preliminarily conclude that the CAN-initiated grafting of Buthylmethacrylate and Acrylic acid onto CMC is also fitted with this kind of rate statement¹⁶⁻¹⁸.

The overall activation energy (E_a) of the graft polymerization reaction was calculated by

using of the Eq. (2) and the slope of the plot $\ln R_g$ versus $1/T$ (Fig. 4) based on Arrhenius relationship [$k_p = A \exp(-E_a/RT)$]. Therefore, E_a for the graft copolymerization was found to be 29.8 kJ/mole.

CONCLUSION

Novel graft copolymer were synthesized by grafting of Simultaneously Acrylic acid and Buthylmethacrylate onto carboxymethylcellulose in the presence of cerium (IV) ammonium nitrate as an efficient initiator in acidified aqueous medium, under inert atmosphere. Empirical polymerization rate showed a first-order dependence on the monomers concentration and a half-order dependence on the initiator concentration. According to the slope of $\ln R_g$ versus $1/T$, 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-PAcA-co-PBMC copolymer is being subjected to further modification to prepare thickeners and flocculants for aqueous systems.

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