

Potassium persulfate induced grafting of polyacrylamide onto kappa-carrageenan

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Abstract:

In this paper, the effect of different reaction conditions on the grafting of acrylamide (AM) onto kappa-carrageenan (kC) using potassium persulfate (KPS) initiator has been studied by determining the grafting parameters. The reactions were carried out under argon atmosphere in a homogenous aqueous medium. After removal of the homopolymer, the graft copolymer was characterized by FTIR spectroscopy. A plausible mechanism of grafting has also been suggested. It was observed that with increasing AM, kC, and KPS concentrations as well as reaction time and temperature the grafting parameters were increased, but further increase of reaction conditions disfavored these parameters.

Keywords: Carrageenan, Acrylamide, Graft copolymerization, Potassium persulfate

Introduction

Considerable interest has been focused on chemical modification by free radical graft copolymerization of hydrophilic and hydrophobic vinyl monomers biopolymers such as polysaccharides^{1,5}. 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 agents^{6,7}

Graft copolymerization can be carried out with different initiator systems. Among them, potassium persulfate, ammonium persulfate, benzoyl peroxide, azo bisisobutyronitrile, and ceric ammonium nitrate are widely used for the synthesis of graft copolymers^{8,9}.

The chosen polysaccharide for modification, i.e. kappa-carrageenan, kC, is the most well-known and most important type of carrageenan family. Carrageenan is a collective term for linear sulfated polysaccharides that are obtained commercially by alkaline extraction

of certain species of red seaweeds¹⁰. Schematic diagram of the idealized structure of the repeat units for the kC, is shown in Figure 1.

A literature survey reveals that no paper has been reported in the case of acrylamide (AM) grafting onto kappa-carrageenan (kC). Therefore, the present report describes graft copolymerization of acrylamide onto this industrial polysaccharide, initiated by potassium persulfate (KPS). The effect of concentration of kC, AM and KPS as well as the reaction time and temperature on the graft copolymerization was studied by determining the grafting parameters.

Experimental

Material

Commercial reagent grade kappa-carrageenan (kC, MW=100000, from Condinson Co., Denmark) was used as received. Pure potassium persulfate and acrylamide were purchased from Merck (Darmstadt, Germany) and used without purification.

Grafting procedure

Graft copolymerization of acrylamide onto kC was carried out with KPS radical initiator under argon atmosphere. In a 100 mL flask, certain amount of kC(0.5-3.0 g) was dissolved in 50 mL of degassed distilled water. The flask was placed in a water bath with desired temperature (50-100 °C). A given amount of monomer, AM (1.0-5.0 g), was added to the flask and the mixture was stirred for 15 min. Then, the initiator (0.03-0.40 g) was added to the mixture and continuously stirred for certain times (30-240 min). An inert gas (argon) was gently bubbled into the reactor to remove the oxygen during the graft copolymerization reaction. The product was then worked up with methanol (200 mL) and dried in oven at 50 °C for 5 h.

Infrared spectroscopy

Fourier transform infrared (FTIR) absorption spectra of finely powdered grafted and ungrafted samples were recorded by an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), using the KBr disc technique.

Evaluation of grafting parameters:

The grafting parameters used to characterize the nature of the copolymer are defined with the weight basis expressions as reported by Fanta⁶. The percentage of grafting ratio (Gr%) stands for the weight percent of the graft copolymer synthetic part (PAM grafted) formed from initial kC used.

$$\text{Grafting ratio}(\%Gr) = \frac{\text{Weight of grafted polymer}}{\text{Weight of substrate}} \times 100 \quad (1)$$

The percentage of grafting efficiency (Ge%) stands for the grafted PAM formed from initial monomer charged.

$$\text{Grafting efficiency}(\%Ge) = \frac{\text{Weight of grafted polymer}}{\text{Weight of polymer formed}} \times 100 \quad (2)$$

The percentage of Add-on (Ad%) is the weight percent of the grafted PAM of the graft copolymer.

$$\text{Add on}(\%Ad) = \frac{\text{Weight of grafted polymer}}{\text{Weight of graft copolymer}} \times 100 \quad (3)$$

The percentage of homopolymer (%Hp) denotes the weight percent of the homopolymer formed from initial monomer charged.

$$\text{Homopolymer}(\%Hp) = 100 - \%Ge \quad (4)$$

Results and discussion

Graft copolymerization mechanism

The mechanism of grafting acrylamide onto kappa-carrageenan using potassium persulfate as a water soluble oxidizing initiator is shown in the Scheme 1. The persulfate initiator is decomposed under heating to generate sulfate anion-radical. The radical abstracts hydrogen from the hydroxyl group of the polysaccharide to form alkoxy radicals on the substrate. So, this persulfate-saccharide redox system is resulted in active centers on the substrate to radically initiate polymerization of acrylamide led to a graft copolymer.

Infrared spectroscopy

Evidence of grafting was obtained by comparison of FTIR spectra of the polysaccharide and the graft copolymer. The FTIR spectrum of pure kC and the final homopolymer-free grafted product, kC-g-PAM, was shown in Figure 2. The bands observed at 844, 910,

1015, and 1222 cm^{-1} can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage, and ester sulfate stretching of kC, respectively (Figure 2a). The broad band at 3200-3400 cm^{-1} is due to stretching of -OH groups of kC. Compared to the spectrum of kC, the IR spectrum of the kC-PAM graft copolymer (Figure 2b) shows a new characteristic absorption band at 1665 cm^{-1} verifying the formation of kC-g-PAM. This peak attributed to C=O stretching in carboxamide functional groups of PAM. The stretching band of -NH overlapped with the -OH stretching band of the kC portion of the copolymer.

The existence of PAM grafting was also monitored gravimetrically. Increase in the mass of kC, after extraction of homopolymer, was taken as evidence for grafting. This weight gain in kC forms the basis for the determination of the grafting parameters.

Effect of reaction conditions on grafting

To optimize the reaction conditions, the effect of concentration of acrylamide, kappa-carrageenan, and potassium persulfate as well as grafting time and temperature was studied in the light of grafting parameters.

Effect of kC concentration

Figure 3 presents the relationship between the kC concentration and the grafting parameters. The increase in the kC amount from 1 to 4 wt% brings about enhancement in grafting, whereas further increase in the substrate decreases the grafting. The initial increase may be due to the availability of more grafting sites, where polysaccharide can be grafted. Subsequent decrease in grafting parameters can be explained on the basis of increase in viscosity of the medium, which hinders the movement of free radicals. This observation is in close agreement with the results obtained by other investigators^{11,13}.

Effect of initiator concentration

The effect of initiator concentration on the grafting parameters was investigated (Figure 4). It is observed that the %Ge and %Gr increased initially on increasing the initiator concentration upto 0.013 mol/L, but decreased with further increase of concentration of KPS. This behavior may be ascribed to the increase of the active free radical sites on the backbone of the kC arising from the attack of radical-anion persulfate. The decrease of grafting parameters may be attributed to the increased number of radicals that led to terminating step via bimolecular collision. Additionally, free radical degradation of kC

substrate is also possible at high KPS levels as described schematically in our previous work¹⁴.

Effect of monomer concentration

Graft copolymerization was studied at various monomer concentrations by keeping other reaction conditions constant. As shown in Figure 5, the grafting parameters were found to be increased by enhancement of acrylamide concentration up to 0.84 mol/L. Beyond this amount, the grafting values were diminished. The initial increase in %Ge and %Gr can be attributed to the increase of monomer concentration in the vicinity of the kC backbone and consequent greater availability and enhancement chances for molecular collisions of the reactants. Subsequent decrease in grafting parameters can be explained on the preferential homopolymerization over graft copolymerization, increasing the viscosity of reaction medium, and increase in the chain transfer to monomer molecules. Similar observations have been reported for the grafting of ethyl acrylate onto cellulose¹⁵, methyl acrylate onto starch¹⁶, and methyl methacrylate onto sodium alginate¹⁷.

Effect of reaction temperature

Figure 6 shows the influence of reaction temperature on grafting. An increase in temperature upto 70 °C increases the grafting parameters. This behavior may be due to the higher rate of diffusion of acrylamide molecules to kC macroradicals. Moreover, higher temperatures increase the solubility of the reactants. On the other hands, since KPS is a thermally dissociating initiator, it reacted very slowly at temperatures lower than its dissociation temperature 70 °C¹⁸. The lower initiating radicals limited the extent of polymerization. The subsequent lower grafting can be explained on the basis of (a) oxidative degradation of kC chains by sulfate radical-anions¹⁴, (b) increasing rate of termination and chain transfer reactions, and (c) decomposition of KPS to give O₂ (a radical scavenger), which reacts with primary free radicals resulting in decreased graft copolymerization reaction⁷.

Using the following empirical formula [19], the rate of graft copolymerization (Rg) was calculated:

$$Rg \left(\text{mol. s}^{-1} . \text{m}^{-3} \right) = \frac{\text{Weight of grafted polymer}}{\text{Molecular weight of monomer} \times [\text{reaction time (s)}] \times \text{volume (m}^3\text{)}} \quad (5)$$

The overall activation energy (Ea) of the graft polymerization reaction was calculated by using of the Equation (5) and the slope of the plot LnRg versus 1/T (Figure 7) based on

Arrhenius relationship [$k_p = A \exp(-E_a/RT)$]. Therefore, E_a for the graft copolymerization was found to be 26.7 kJ/mole.

Effect of reaction time

The effect of reaction time on graft copolymerization of acrylonitrile onto kC backbones was shown in Figure 8. The grafting parameters increased versus time up to 120 min and then, it is 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 kC surface, may be other possible reasons for the diminished grafting at longer reaction times. Similar time dependency of grafting parameters was reported by others^{20,21}.

Conclusion

In the present investigation, the effect of concentration of kC, KPS and AM, along with reaction time and temperature of AM grafting onto kC backbones was studied to achieve the maximum grafting parameters. It may be found from the related curves 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. The optimum reaction conditions were found to be as follows: kC 4 wt%, AM 0.84 mol/L, KPS 0.013 mol/L, reaction temperature 70 °C, and reaction time 120 min. FTIR spectroscopy and gravimetric analysis clearly illustrate the graft copolymerization do takes place. According to the slope of $\ln R_g$ versus $1/T$, the overall activation energy for graft copolymerization reaction was estimated to be 26.7 kJ/mol. As an extension of this work, the kC-g-PAM copolymer is being subjected to further modification to prepare thickeners and flocculants for aqueous systems.

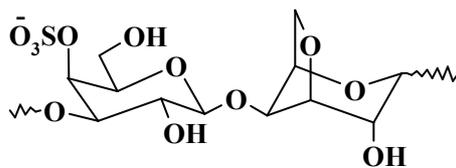


Figure 1. Repeating disaccharide unit of kappa-carrageenan (kC)

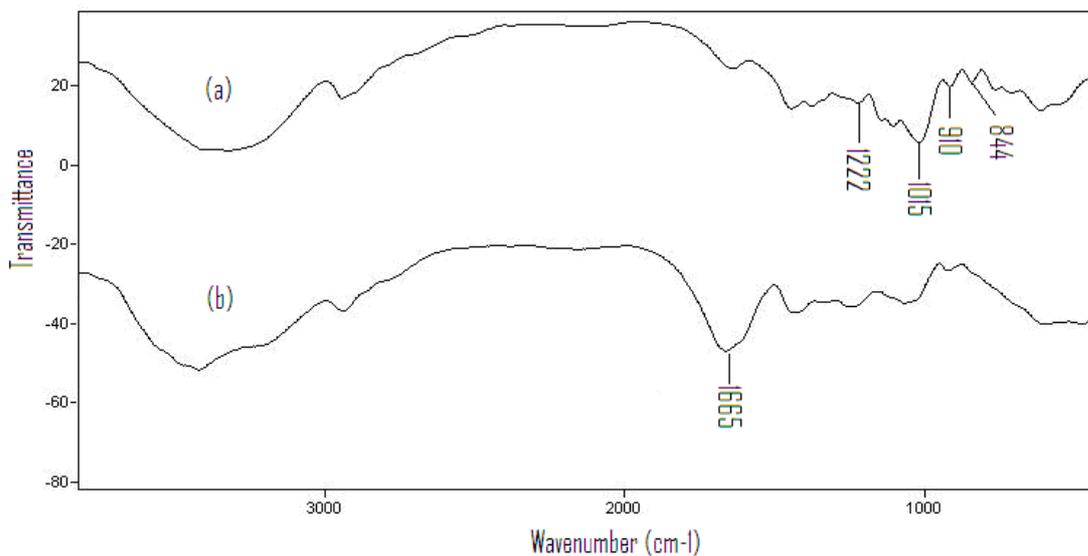


Figure 2. FTIR spectra of kC (a) and graft copolymer, kC-g-PAM (b).

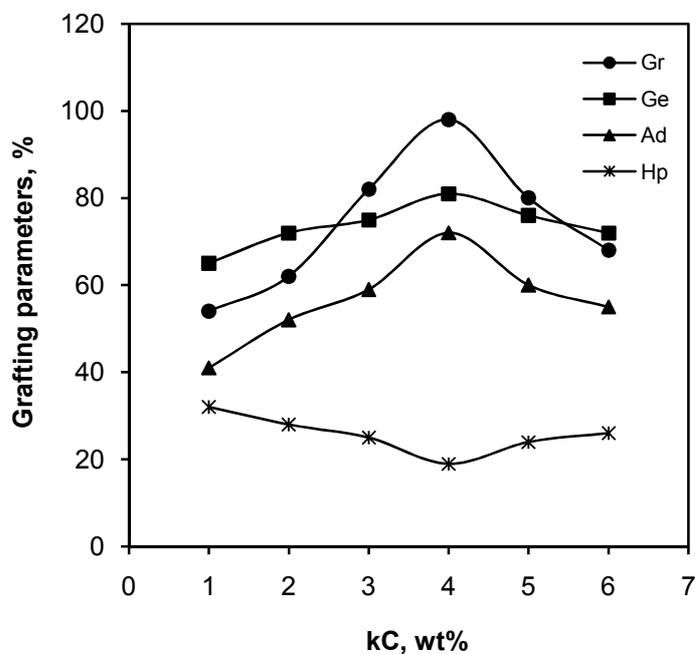


Figure 3. Grafting parameters as functions of kC concentration.

Reaction conditions: KPS 0.009 M, AM 0.7 mol/L, temperature 60°C, time 90 min.

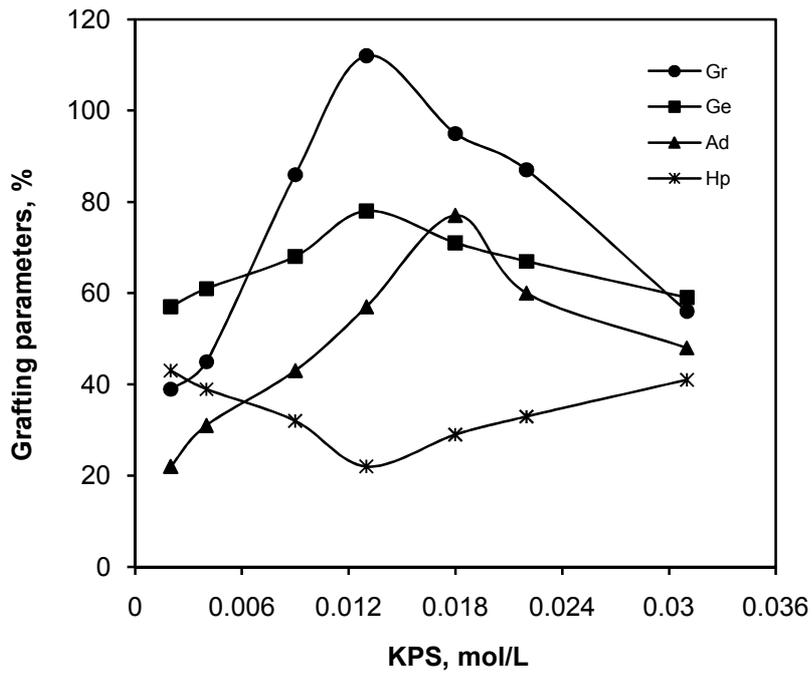


Figure 4. Effect of initiator concentration on the grafting parameters.

Reaction conditions: kC 4 wt%, AM 0.7 mol/L, temperature 60°C, time 90 min.

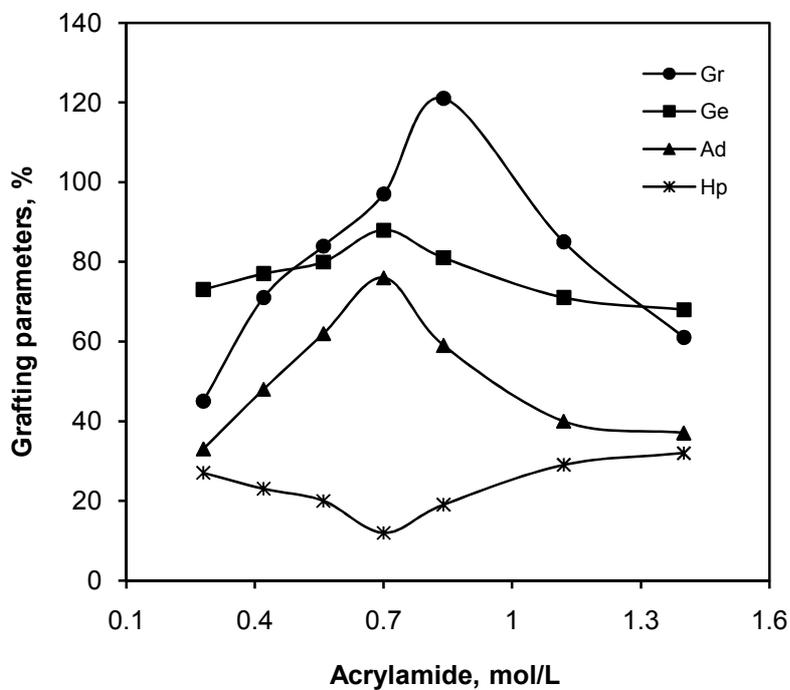


Figure 5. Effect of the monomer concentration on the grafting parameters.

Reaction conditions: kC 4 wt%, KPS 0.013 mol/L, temperature 60°C, time 90 min.

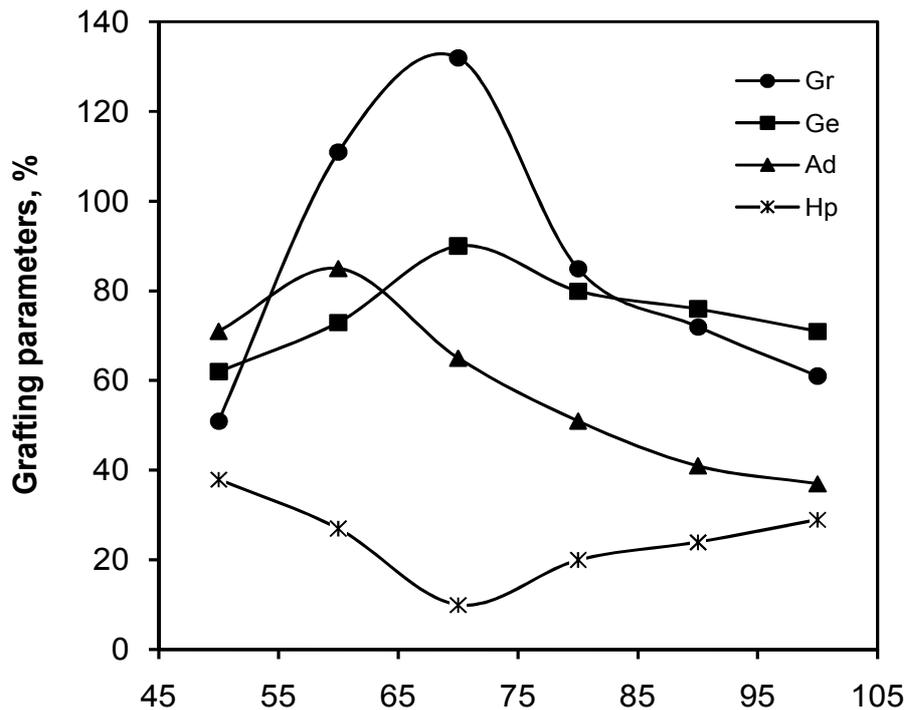


Figure 6. Effect of the reaction temperature on the grafting parameters.
 Reaction conditions: kC 4 wt%, KPS 0.013 mol/L, AM 0.84 mol/L, time 90 min.

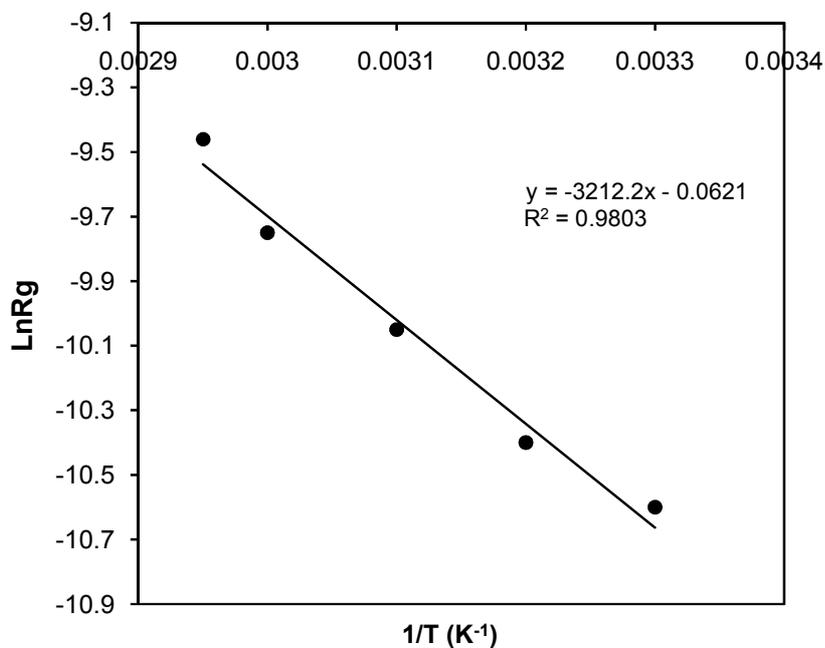


Figure 7. Plot of LnRg versus 1/T for estimating the activation energy of the graft polymerization reaction.

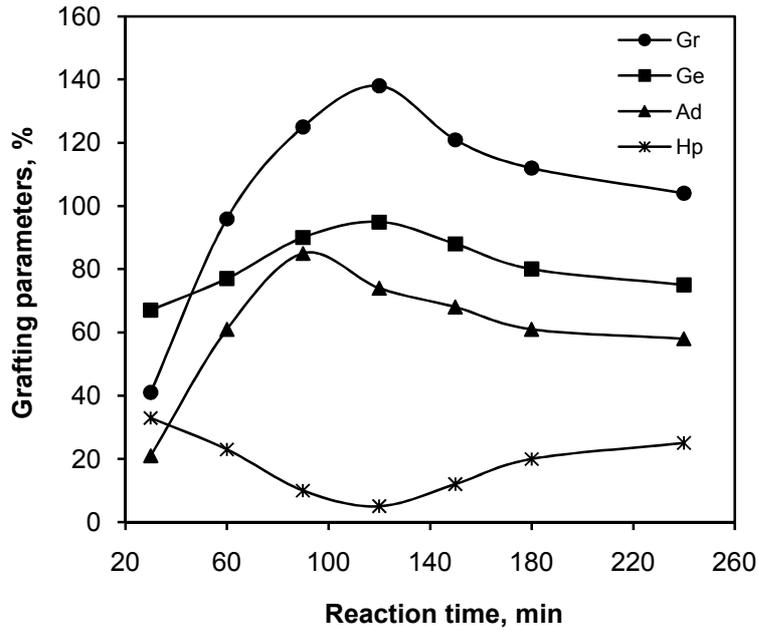
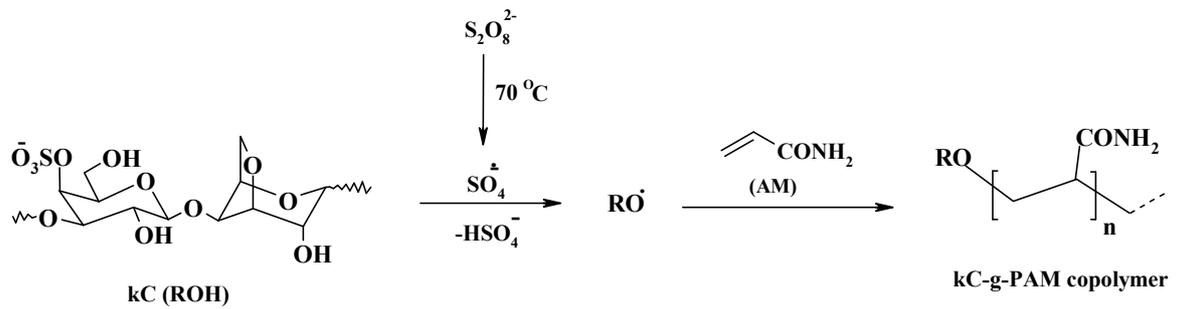


Figure 8. Effect of the reaction time on the grafting parameters.

Reaction conditions: kC 4 wt%, KPS 0.013 mol/L, AM 0.84 mol/L, temperature 70°C.



Scheme 1. A brief proposed mechanism for KPS-induced grafting of poly(acrylamide) onto kappa-carrageenan.

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