Asian Journal of Chemistry; Vol. 24, No. 7 (2012), 3187-3190

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Graft Copolymerization of Acrylamide Monomer onto Kappa-Carrageenan and Determination of the Grafting Parameters

FATEMEH SOLEIMANI[1], MOHAMMAD SADEGHI[2,*] and HADIS SHAHSAVARI[1]

[1]Young Researchers Club, Khorramabad Branch, Islamic Azad University, Khorramabad, Iran
[2]Department of Chemistry, Science Faculty, Islamic Azad University, Arak Branch, Arak, Iran

*Corresponding author: Fax: +98 861 3670017; Tel: +98 916 1613256; E-mail: m-sadeghi@iau-arak.ac.ir

(*Received*: 6 August 2011; *Accepted*: 22 February 2012) AJC-11097

The polysaccharide, kappa-carrageenan (kC), has been chemically modified by graft copolymerization of acrylamide (AAm) in an aqueous medium using ceric ammonium nitrate as an initiator under argon atmosphere. Evidence of grafting was obtained by comparison of FTIR spectra of kappa-carrageenan and homopolymer-free kC-*g*-poly(AAm) as well as solubility characteristics and gravimetric analysis of the products. The optimum reaction conditions affording maximum grafting ratio and add-on value have been determined.

Key Words: Carrageenan, Grafting, Acrylamide, Ceric ammonium nitrate.

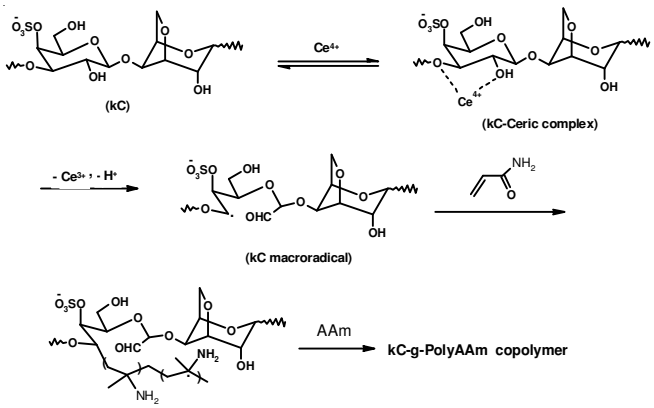
INTRODUCTION

Graft copolymerization of hydrophilic and hydrophobic vinyl monomers is a well-known technique employed by polymer chemists for significantly modifying the chemical and physical properties of the synthetic or natural starting materials with minimum degradation of the original properties[1-4]. Graft copolymers are prepared by first generating free radicals on the polysaccharide backbone and then allowing these radicals to serve as macroinitiators for the vinyl monomers. These biodegradable and low cost graft copolymers, with new properties can be used in many applications such as textiles, paper industry, agriculture, medical treatment, in petroleum industry as flocculants and thickening agents[2] and also development of selective permeable membranes, sorption agents and in fabrication of drug delivery systems[4,5].

Grafting can be performed using free radical initiators, redox systems or photochemical process. Cerium in its tetravalent state (Ce^{4+}) is a versatile oxidizing agent that through various redox reactions with many different organic substrates can create free radicals capable of initiating vinyl polymerizations. Since the discovery of ceric ammonium nitrate as an initiator by Mino and Kizerman[6], it has been widely used by many investigators for initiating graft copolymerization of vinyl monomers onto various natural and synthetic polymers. For example, graft copolymerization of acrylamide, acrylonitrile and methacrylonitrile were performed using Ce(IV) as an initiator.

Though much work has been reported on the grafting of 2-hydroxyethylmethacrylate (HEMA) onto various polysaccharides, but a literature survey reveals that no paper has been published in the case of 2-hydroxyethylmethacrylate grafting onto kappa-carrageenan (kC). Therefore, the present investigation deals with the detailed study of some major factors which affect graft copolymerization of 2-hydroxyethylmethacrylate onto kappa-carrageenan, initiated by ceric ammonium nitrate in aqueous medium with a view to elucidate the grafting mechanism[7-11].

The chosen polysaccharide for modification, *i.e.* kappa-carrageenan, is the 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 seaweeds. Schematic diagram of the idealized structure of the repeat units for the kappa-carrageenan, is framed in **Scheme-I**.



Scheme-I: A brief proposed mechanism for ceric-induced grafting of polyacrylamide onto kappa-carrageenan

Carrageenan is not a single biopolymer but a mixture of water-soluble, linear, sulfated galactans. They are composed of alternating 3-linked β-D-galactopyranose (G-units) and 4-inked β-D-galactopyranose (D-units) or 4-linked 3,6-anhydrogalactose (DA-units) forming the "ideal" disaccharide-repeating unit of carrageenans. The sulfated galactans are classified according to the presence of the 3,6-anhydrogalacto-pyranose on the 4-linked residue and the position and number of sulfate groups. The corresponding IUPAC name and letter code for kappa-carrageenan are carrageenose 4′-sulfate and G4S-DA.

EXPERIMENTAL

The polysaccharide, kappa-carrageenan (kC, from Condinson Co., Denmark); ceric ammonium nitrate (CAN, from Fluka), acrylamide (AAm, from Merck) were of analytical grade and were used as received. All other chemicals were of analytical grade.

Grafting procedure: Graft copolymerization of acrylamide onto kappa-carrageenan was carried out with ceric ammonium nitrate radical initiator under argon atmosphere. In a 50 mL flask, certain amount of kappa-carrageenan (0.3-1.5 g) was dissolved in 30 mL of degassed distilled water. The flask was placed in a water bath with desired temperature (35-70 ºC). A given amount of monomer, acrylamide (0.5-3.5 g), was added to the flask and the mixture was stirred for 15 min. Then the initiator solution (1.8-5.5 mL of 0.1 mol/L acidic solution of calcium ammonium nitrate) was added to the mixture and continuously stirred for certain times (60-180 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 ºC for 5 h.

Homopolymer extraction: The graft copolymer, kC-*g*-poly(AAm), was freed from polyacrylamide homopolymer, by pouring 0.50 g of the product in 50 mL of mixture dimethyl formamide-ethanol solution. The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer by filtration of the kC-*g*-poly(AAm) copolymer, the product was washed with methanol and dried in oven at 50 ºC to reach a constant weight.

Infrared spectroscopy: The samples were powdered and mixed with KBr to make pellets. Spectra were taken using an ABB Bomem MB-100 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Grafting mechanism and spectral characterization: A general reaction mechanism for acrylamide grafting onto kappa-carrageenan backbones is shown in **Scheme-I**. At the first step, a complex between the Ce^{4+} ion with the oxygen atom at the C-3 position and the hydroxyl group at the C-2 position was formed. This ceric-kC complex is then dissociated to produce kappa-carrageenan macroradicals. The monomer molecules, which are in vicinity of the macroradical sites, become acceptor of kappa-carrageenan radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighbouring molecules leading to propagation. These grafted chains are terminated by coupling to give the graft copolymer[4,5,7,8].

FTIR analysis: Structural changes of kappa-carrageenan and its graft copolymer were confirmed by FTIR spectroscopy. The FTIR spectrum of kappa-carrageenan and the final grafted copolymer, kC-*g*-polyacrylamide, was shown in Fig. 1. The IR spectrum of kappa-carrageenan shows peaks at 840, 914, 1019 and 1225 cm^{-1} could be related to β-D-galactopyranose-4-sulfate, 3,6-anhydro-β-D-galactopyranose, glycosidic linkage and ester sulfate stretching of kappa-carrageenan, respectively (Fig. 1a). The broad band at 3400-3200 cm^{-1} is due to stretching of -OH groups of kappa-carrageenan. In the spectrum of homopolymer-free kC-*g*- polyacrylamide, the strong peak at 1660 cm^{-1} could be assigned to the C=O stretching in the ester group from the polyacrylamide grafted onto kappa-carrageenan backbones.

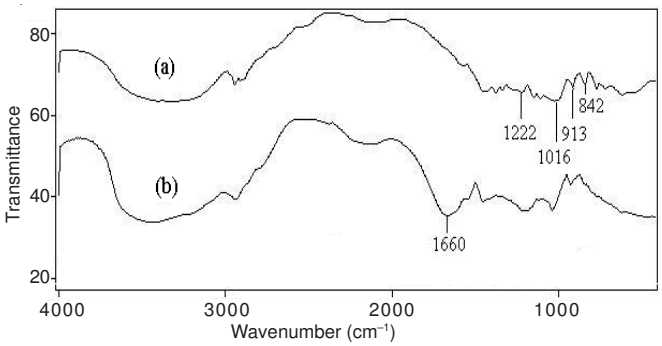


Fig. 1. FTIR spectra of pure kC (a) and kC-*g*-PAAm (b)

Solubility test: To obtain an additional evidence of grafting, solubility difference between the grafted and the non-grafted polymer was used. Kappa-carrageenan and polyacrylamide are soluble in water and DMF-ethanol, respectively. When a reaction product was extracted with DMF-ethanol and alternatively with water for 24 h, an insoluble solid still remained. A physical mixture of kappa-carrageenan and polyacrylamide 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 kappa-carrageenan substrate and polyacrylamide macromolecules. In addition to the formation of graft copolymers, crosslinking between the chains of kappa-carrageenan may also take place. This was evident by the reaction between kappa-carrageenan and the initiator, in the absence of monomers, giving a product with reduced solubility (unpublished data).

Moreover, because of insolubility of the graft copolymer and polyacrylamide in water and in the acrylamide monomer, respectively, the polymerization reaction proceeds as a heterogeneous process and the formed copolymer precipitate during the process. This observation practically proves that the grafting reaction was performed[9-12].

Gravimetric analysis: The graft copolymerization reaction was monitored gravimetrically. Increase in the mass of kappa-carrageenan, after extraction of homopolymer, was taken as evidence for grafting. This weight gain in kappa-carrageenan forms the basis for the determination of the grafting parameters.

Optimization of polymerization: Since polymerization variables determine the extent of grafting and homopolymer amount, certain factors affecting the grafting parameters were investigated to achieve the optimum condition of polymerization. Therefore, we optimized the grafting of acrylamide onto kappa-carrageenan in homogenous aqueous media by changing temperature, the initial concentration of monomer, initiator and the relative amount of the substrate. Within the range of the amount of the reactants used, our preliminary studies showed no considerable dependence between the reaction time and the grafting extent[13].

The conversion as well as the grafting parameters, *i.e.* homopolymer content (Hp), grafting ratio (Gr) and the grafting add-on values was calculated using the following equations:

$$\text{Grafting (Gr)} = W_3/W_0 \quad (1)$$

$$\text{Homopolymer content (Hp)} = W_2/(W_2+W_3) \quad (2)$$

$$\text{Add-on} = (W_3-W_0)/W_3 \quad (3)$$

where, W_0, W_1, W_2, W_3 and W_4 are weight of the initial substrate, the monomer charged, the homopolymer extracted, the homopolymer-free graft copolymer and polyacrylamide side-chains separated, respectively.

Effect of initiator concentration: The grafting dependence on ceric ammonium nitrate concentration can be concluded from Fig. 2. The highest grafting ratio (321 %) was achieved at 0.0006 mol/L of ceric ammonium nitrate where homopolymer content was 5 %. Increased ceric ammonium nitrate concentration resulted in more radical sites on the polysaccharide backbone that in turn led to higher grafting ratio and add-on values and lower homopolymer formation. However, since the ceric ammonium nitrate initiator solution is used as dilute HNO_3, at ceric ammonium nitrate concentration higher than 0.0006 mol/L, a more acidic pH probably causes partially termination of the macroradicals on kappa-carrageenan. As a result, increased free radicals on PE are compensated by partial termination of the macroradicals. Thus grafting ratio and add-on values were diminished at higher amounts of the initiator[10,14].

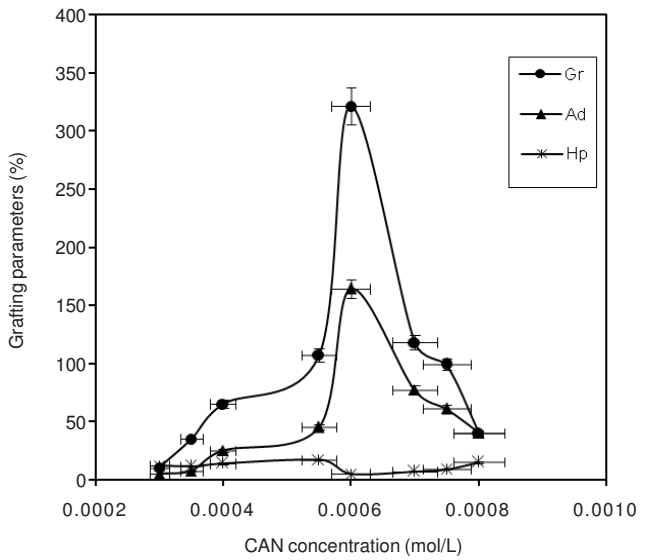


Fig. 2. Grafting per cent variances with concentration of ceric ammonium nitrate (CAN) variance

Effect of temperature: To study the influence of the reaction bath temperature on the grafting parameters, the grafting of acrylamide onto kappa-carrageenan was carried out at six temperature ranging from 35 to 70 ºC. The results are given in Fig. 3. Grafting percentage (% Gr) is increased with increasing the temperature from 35 to 50 ºC and then decreased. At 50 ºC, maximum grafting (Gr 297 %), minimum homopolymer content (11 %) and highest add-on value (104 %) was obtained. Improvement of grafting up to 50 ºC can be attributed to the following factors: increased the number of free radicals formed on the Pectin backbone, increased propagation of the graft copolymerization onto kappa-carrageenan, enhanced diffusion of monomer and initiator into and onto backbone structure and increased in mobility of the monomer molecules and their higher collision probability with the backbone macroradicals[15-17]. However, grafting was decreased as the bath temperature was raised beyond 50 ºC. This can be accounted for in terms of chain radical termination at higher temperatures. Premature termination of growing chains and instability of the ceric-saccharide complex are presumably another reasons for reduced amount of grafting beyond 50 ºC. The polyacrylamide homopolymer formation is minimal at the bath temperature of 50 ºC.

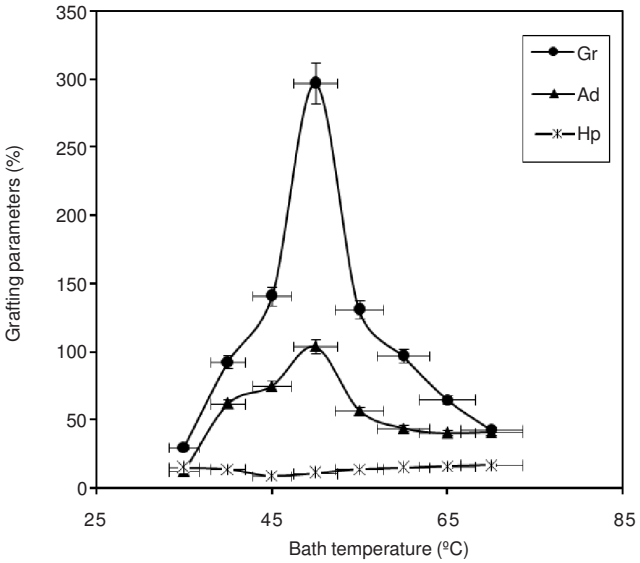


Fig. 3. Grafting per cent variances with temperature variance

Effect of acrylamide concentration: The effect of monomer amount on the grafting reaction was studied at various concentrations of acrylamide while other influential factors were unchanged. The grafting parameter variations are changed by the amount of charged monomer. The results are given in Fig. 4. The grafting extent is significantly increased due to more availability of monomer for grafting. However, beyond a certain grafting ratio value, *i.e.*, 346 % at acrylamide 1.5 g, the trend is inversed. The conversion and the grafting efficiency (Ge) are decreased and homopolymer content is increased noticeably from 11 to 17 percent[18]. Thus, acrylonitrile in an amount of acrylamide 1.5 g was recognized as an optimum monomer concentration. Once the monomer units are added, an excess of monomer can only increase the optimum volume of the reaction mixture. The resulting reduced relative

concentration of the initiator and substrate leads to decreased conversion and grafting efficiency[17,19,20].

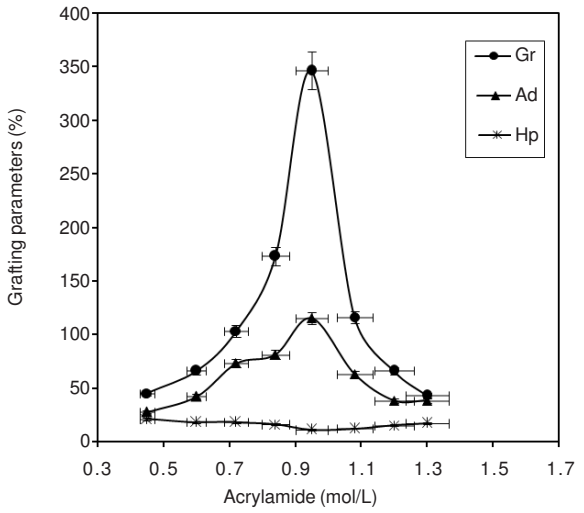


Fig. 4. Grafting per cent variances with amount of acrylamide monomer variance

Effect of polysaccharide concentration: The related to the grafting dependence on kappa-carrageenan amount is summarized in Fig. 5. Maximum grafting and the lowest homopolyacrylamide formation was observed at 0.66 g kappa-carrageenan, while others reactants including, monomer, initiator and temperature were kept constant. Beyond this value, both grafting ratio and add-on values are considerably reduced[21]. This behaviour is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher concentration of the substrate (from 0.4 to 0.66 g kappa-carrageenan). However, upon further increase in the substrate concentration, increase in the reaction medium viscosity restricts the movements of macroradicals leading to decreased grafting ratio and add-on values. It also may be attributed to deactivation of the macroradical growing chains (*e.g.*, by transfer reactions, combination and/or interaction with the primary radicals) soon after their formation[9,20].

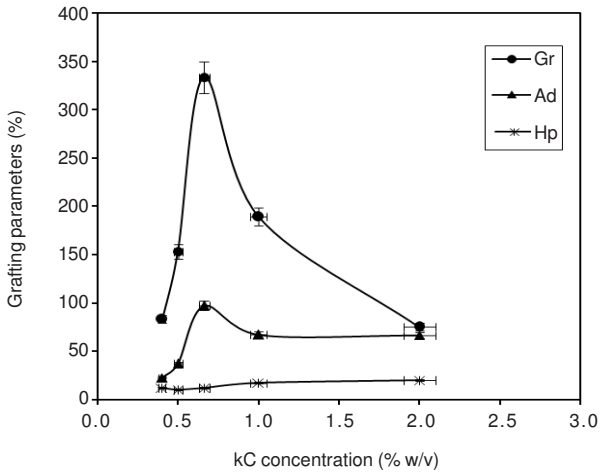


Fig. 5. Grafting per cent variances with amount of kappa-carrageenan variance

Conclusion

A doubly modified polysscharide, kC-*g*-polyacrylamide, was prepared using ceric-initiated graft polymerization of acrylamide (AAm) onto kappa-carrageenan. The synthetic conditions were systematically optimized through studying the influential factors including temperature, concentration of the initiator, the monomer acrylamide and the substrate kappa-carrageenan. The effect of the individual factors was investigated by calculating the grafting parameters, *i.e.*, grafting ratio (Gr), add-on value and homopolymer content (Hp). Under optimum conditions (kC 0.66g, AAm 1.5 g, ceric ammonium nitrate 0.0006 mol/L, reaction bath temperature 50 ºC), the grafting parameters were achieved as 346, 104,1 and 5 % respectively.

REFERENCES

1. S.J. Metz, W.J.C. Van de Ven and J. Potreck, *J. Membrane Sci.*, **251**, 29 (2005).
2. J.H. Ye, J.J. Dong, J.L. Lu, X.Q. Zheng, J. Jin, H. Chen and Y.R. Liang, *Carbohyd. Polym.*, **81**, 441 (2010).
3. M. Sadeghi and M. Yarahmad, *Afr. J. Biotechnol.*, **10**, 12265 (2011).
4. M. Sadeghi, *Turk. J. Chem.*, **35**, 723 (2011).
5. M. Sadeghi and H. Hosseinzadeh, *J. Chil. Chem. Soc.*, **55**, 497 (2010).
6. G. Mino and S. Kaizerman, *J. Polym. Sci.*, **31**, 242 (1958).
7. M. Sadeghi and H. Hosseinzadeh, *Turk. J. Chem.*, **34**, 739 (2010).
8. A. Pourjavadi, H. Hosseinzadeh and M. Sadeghi, *J. Comp. Mater.*, **41**, NO.17 (2007).
9. M. Sadeghi and H. Hosseinzadeh, *J. Appl. Polym. Sci.*, **108**, 1142 (2008).
10. M. Sadeghi and H. Hosseinzadeh, *Asian J. Chem.*, **22**, 6734 (2010).
11. M. Sadeghi and K. Monavar, *Asian J. Chem.*, **23**, 5253 (2011).
12. M. Sadeghi, M. Nasrolahi, *Asian J. Chem.*, **23**, 5295 (2011).
13. B. Singh, N. Chauhan and S. Kumar, *Carbohyd. Polym.*, **73**, 446 (2008).
14. P. Lv, Y. Bin, Y. Li, R. Chen, X. Wang and B. Zhao, *Polymer*, **50**, 5675 (2009).
15. A. Pourjavadi, M.J. Zohuriaan-Mehr, A. Pooraghaberar and H. Hosseinzadeh, *J. Polym. Mater.*, **21**, 351 (2004).
16. R.E. Kirk and D.F. Othmer, Encyclopedia of Chemical Technology, John Wiley & Sons, New York, edn. 4 (1992).
17. B.N. Mishra, J. Kishore, M. Kanthwal and I.K. Mehta, *J. Polym. Sci. Part A: Polym. Chem.*, **24**, 2209 (1986).
18. K.C. Gupta, S. Sahoo and K. Khandekar, *Biomacromolecules*, **3**, 1087 (2002).
19. A. Pourjavadi and M.J. Zohuriaan-Mehr, *Starch/Starke*, **54**, 140 (2002).
20. M.J. Zohuriaan-Mehr, A. Pourjavadi and M. Sadeghi, *Iran. Polym. J.*, **14**, 131 (2005).
21. F. Carrillo, B. Defays and X. Colom, *Eur. Polym. J.*, **44**, 4020 (2008).