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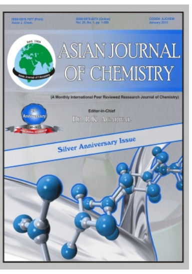

Graft Polymerization of Acrylonitrile-Sucrose and Determination of the Grafting Parameters

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Graft copolymerization of acrylonitrile onto sucrose was carried out under argon atmosphere in a homogeneous aqueous medium by using ceric ammonium nitrate as an initiator. A tentative mechanism is proposed to explain the generation of radicals and the initiation. 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.

Key Words: Sucrose, Acrylonitrile, Graft copolymerization, Ceric ammonium nitrate.

INTRODUCTION

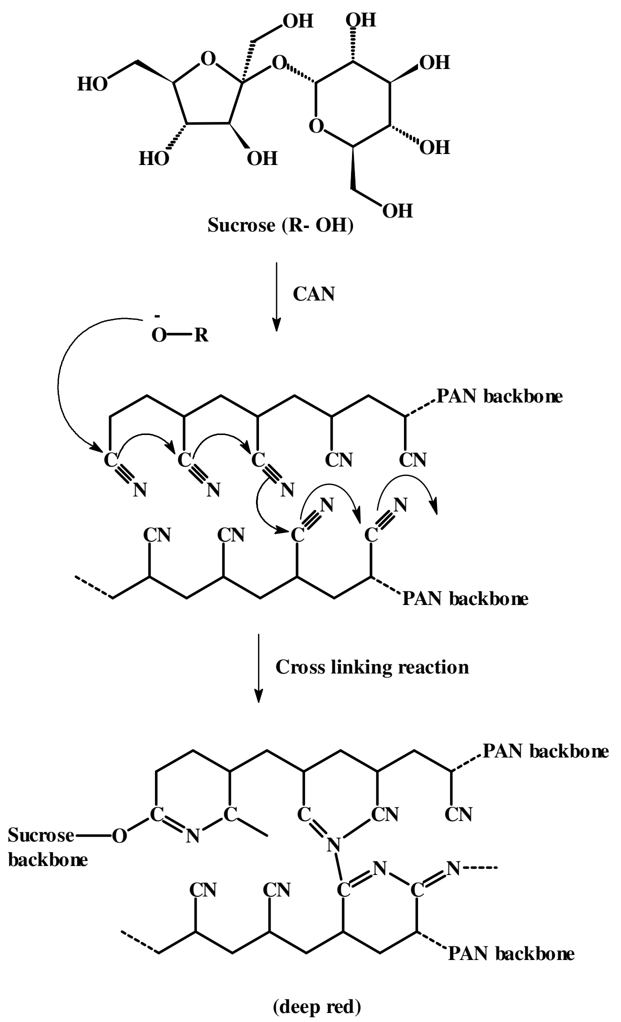
During the past decades, considerable research was being carried out on the graft copolymerization of hydrophilic and hydrophobic vinyl monomers onto polysaccharides and disaccharides[1-5]. These biodegradable and low cost graft copolymers, with new properties, can be used in many applications such as textiles, paper industry, agriculture, medical treatment and also in petroleum industry as flocculants and thickening agents[1-3,6-9]. Free radical graft copolymerization was usually carried out by using various initiators such as ammonium persulfate, benzoyl peroxide and azoisobutyronitrile. Mino and Kaizerman[10] for the first time utilized ceric ammonium nitrate (CAN) as a very effective redox initiator. Ceric ammonium nitrate 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[11,12]. Ceric ions have been also used to graft copolymerized some vinyl monomers including acrylonitrile[13], methyl acrylate and methyl methacrylate and acrylamide[14-16] onto sodium alginate. In addition, ceric ion was recently used to graft copolymerization of acrylamide onto carboxymethyl starch[17] and carboxymethylcellulose[18]. Starch-g-poly(methacrylonitrile)[19] and cyanoethylcellulose-g-poly(acrylonitrile) was also prepared by this method. But a literature survey reveals that no paper has been reported in the case of acrylonitrile (AN) grafting onto disaccharides. Therefore, in the present work, we attempted to modify sucrose by free radical graft copolymerization of acrylonitrile. The grafting reaction was carried out in an aqueous solution by ceric ammonium nitrate as a redox initiator in dilute nitric acid solution. The effect of concentration of sucrose, polyacrylonitrile and ceric ammonium nitrate as well as the reaction time and temperature on the graft copolymerization was studied by determining the grafting parameters.

EXPERIMENTAL

The disaccharide sucrose was purchased from Merck Chemical Co. (Germany). Acrylonitrile monomer (Merck) was distilled before use. Double distilled water was used for the copolymer preparation.

Graft copolymerization procedure: A weighed amount of disaccharide 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 ºC. 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 acrylonitrile 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 ceric ammonium nitrate was added and the graft copolymerization reaction was conducted for 2 h. Finally, the resulted product was precipated by pouring the reaction mixture solution into 250 mL of methanol and the precipitate was filtered and repeatedly washed with methanol. A general reaction mechanism for sucrose-g-poly(acrylonitrile) copolymer formation is shown in **Scheme-I**.

Homopolymer extraction: The graft copolymer, namely sucrose-g-polyacrylonitrile, was freed from polyacrylonitrile (PAN) homopolymer, by pouring 0.80 g of the product in 50 mL of dimethylformamide solution. The mixture was stirred gently at room temperature for 48 h. After complete removal



Scheme-I: General reaction mechanism for graft copolymerization of acrylonitrile onto sucrose backbone in the presence of ceric(IV) ion

of the homopolymer, the sucrose-g-polyacrylonitrile was filtered, washed with methanol and dried in oven at 50 ºC to reach a constant weight.

RESULTS AND DISCUSSION

Characteristic grafting parameters: The percentage of grafting ratio (Gr %), grafting efficiency (Ge %), add-on (Ad %), total conversion (Ct %) and homopolymer (Hp %) were evaluated with the following weight-basis expressions as reported by Fanta[1]:

$$\text{Grafting ratio (\%)} = \frac{\text{Polyacrylonitrile grafted}}{\text{Initial sacurose}} \times 100 \quad (1)$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Polyacrylonitrile grafted}}{\text{Monomer charged}} \times 100 \quad (2)$$

$$\text{Add-on (\%)} = \frac{\text{Polyacrylonitrile grafted}}{\text{Graft copolymer}} \times 100 \quad (3)$$

$$\text{Homopolymer (\%)} = (1 - \text{Ge}) \times 100 \quad (4)$$

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

Optimization of the reaction conditions: In the present investigation, the effect of concentration of sacurose, ceric ammonium nitrate and acrylonitrile, 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 grafting ratio, grafting efficiency and add-on. The reason is the similar concepts applied for defining the grafting parameters (eqns. 1-4).

Effect of initiator concentration: The effect of concentration of ceric ammonium nitrate on graft polymerization was studied by changing its concentration from 0.0002-0.0009 mol/L (Fig. 1). It was observed that with increasing ceric ammonium nitrate concentration, from 0.0002-0.0005 mol/L, both grafting ratio % and grafting efficiency % were increased. Further increase of concentration of ceric ammonium nitrate beyond 0.0005 mol/L disfavored the grafting parameters. The initial increase in grafting ratio % and grafting efficiency % may be attributed to increased number of active free radical sites on the sucrose backbone. The decrease of grafting parameters at higher concentration of ceric ammonium nitrate may be due to (a) oxidative degradation of sucrose chains by excess Ce^{4+} 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 others[18,19].

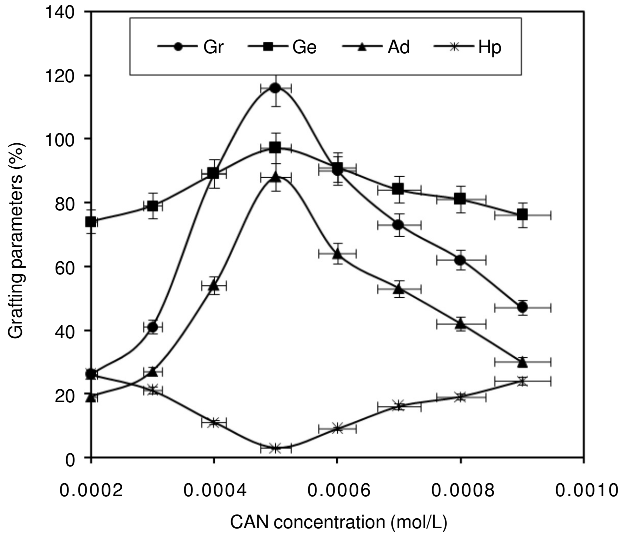


Fig. 1. Variation of grafting parameters for the graft polymerization of acrylonitrile (AN) onto sucrose *versus* different concentration of the initiator (CAN)

Effect of monomer concentration: The effect of monomer amount on the grafting reaction was studied at various concentrations of acrylonitrile while other influential factors were unchanged. The grafting parameter variations are changed by the amount of charged monomer (Fig. 2). The grafting extent is significantly increased due to more availability of monomer for grafting. However, beyond a certain grafting ratio value, *i.e.*, 122 % at 9 mol//L acrylonitrile, the trend is inversed. The conversion and the grafting efficiency (Ge) are decreased and homopolymer content is increased noticeably from 11-45 %. Thus, acrylonitrile in an amount of 1.6 g (9 mol/L) 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. Needless to say, the increase in the chain transfer to monomer molecules may be other possible reason for the diminished grafting at higher acrylonitrile concentrations. Similar observations have been reported for the grafting of ethyl acrylate onto cellulose[20] and methyl acrylate onto starch[21].

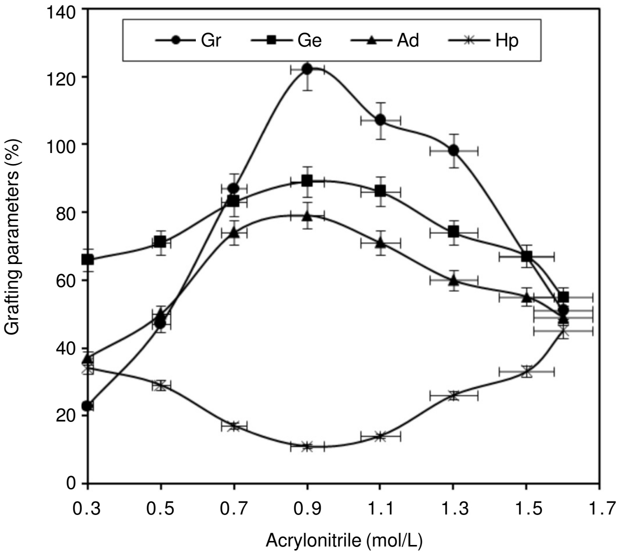


Fig. 2. Variation of grafting parameters for the graft polymerization of acrylonitrile (AN) onto sucrose *versus* different concentration of the momomer

Effect of sucrose concentration: The effect of sucrose concentration on graft copolymerization was depicted in Fig. 3. With increasing the sucrose amount, more reactive grafting sites are formed which is favorable for grafting. This can account for initial increment in grafting parameters up to 1.2 % w/v of sucrose 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 investigators[22-24].

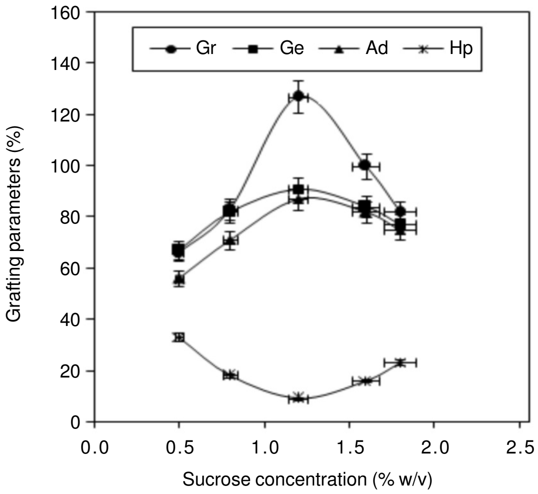


Fig. 3. Variation of grafting parameters for the graft polymerization of acrylonitrile (AN) onto sucrose *versus* different concentration of substrate

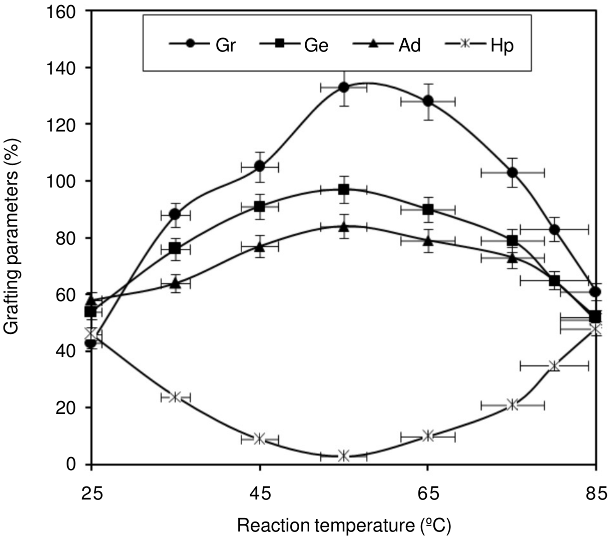


Fig. 4. Variation of grafting parameters for the graft polymerization of acrylonitrile (AN) onto sucrose *versus* different reaction temperature

Effect of reaction temperature: The grafting reactions were carried out at different temperatures between 25 and 85 ºC, keeping the other variables constant. As shown in Fig. 4, it is found that grafting ratio % and add-on % increase initially and then decrease to some extent with further increase in temperature. This is attributed to the fact that increasing the temperature favours the activation of macroradicals as well as accelerates the diffusion and mobility of the monomers from the aqueous phase to the backbone. However, a further increase in temperature decreases grafting ratio % and add-on parameters, which can be ascribed both to the acceleration of termination reaction and to the increased chance of chain transfer reaction, accounting for the increase in the amount of homopolymers. This observation indicates that the optimal reaction temperature is 55 ºC. Similar behaviour was observed in the case of grafting of acrylic acid onto methyl cellulose[24] and acrylamide onto xanthan gum[25].

Effect of reaction time: Fig. 5 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 sucrose surface, may be other possible reasons for the diminished grafting at longer reaction times. Similar time dependency of grafting parameters was reported by others[26,27].

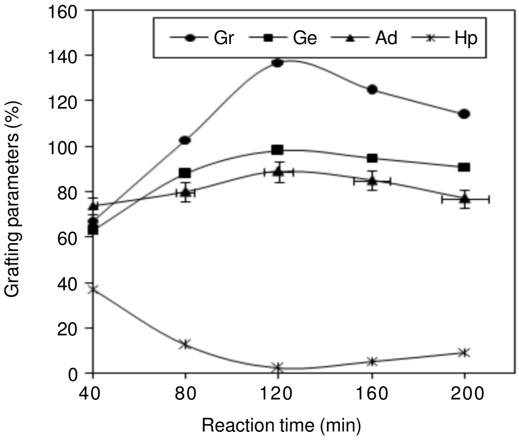


Fig 5. Variation of grafting parameters for the graft polymerization of acrylonitrile (AN) onto sucrose *versus* different reaction time

It should be pointed out that, as shown in the Figs. 6-10, the magnitudes of changes of grafting ratio and grafting efficiency differ drastically, *i.e.*, the changes of grafting ratio is much more than grafting efficiency in the case of every reaction variable. This difference implies that the 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 grafting ratio much more than on grafting efficiency. In other word, the parameter grafting efficiency ratio is more sensitive to the initial reactants than grafting efficiency.

Conclusion

Graft copolymerization was employed as an important technique to obtain a chemically modified natural disaccharide, sucrose. In this paper, a novel graft copolymer were synthesized by grafting of acrylonitrile onto sucrose 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 disaccharide, reaction time and temperature was studied in detail. The optimum reaction conditions were found to be ceric ammonium nitrate 0.0005 mol/L, acrylonitrile 0.90 mol/L, sucrose 1.2 % 2/v, reaction temperature 55 ºC and reaction time 2 h. Under the optimized conditions the grafting parameters were calculated to be grafting ratio 137 %, grafting efficiency 98 %, add-on 89 % and homopolymer 2 %.

REFERENCES

1. G.F. Fanta, In ed.: R.J. Cerasa, In Block and Graft Copolymerization, Wiley, London (1973).
2. A. Hebeish and J.T. Guthrie, In The Chemistry and Technology of Cellulosic Copolymers, Springer-Verlag, Berlin (1981).
3. V.D. Athawale and S.C. Rathi, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C39**, 445 (1999).
4. T. Sun, P. Xu, Q. Liu, J. Xue and W. Xie, *Eur. Polym. J.*, **39**, 189 (2003).
5. Y. Cao, X. Qing, J. Sun, F. Zhou and S. Lin, *Eur. Polym. J.*, **38**, 1921 (2002).
6. R.P. Singh, In eds.: P.N. Prasad, J.E. Mark and T.J. Fal, Polymers and Other Advanced Materials, Emerging Technologies and Business Opportunities, Plenum, New York, p. 227 (1995).
7. N. Bicak, D.C. Sherrington and B.F. Senkal, *React. Func. Polym.*, **41**, 69 (1999).
8. L.M. Zhang and B.W. Sun, *J. Appl. Polym. Sci.*, **74**, 3088 (1999).
9. W.F. Lee and G.Y. Haung, *Polymer*, **37**, 4389 (1996).
10. G. Mino and S. Kaizerman, *J. Polym. Sci.*, **31**, 212 (1958).
11. D.R. Patil and G.F. Fanta, *J. Appl. Polym. Sci.*, **47**, 1765 (1993).
12. L. Rahman, S. Silong, W.M. Zin, M.Z.A. Rahman, M. Ahmad and J. Haron, *J. Appl. Polym. Sci.*, **76**, 516 (2000).
13. S.B. Shah, C.P. Patel and H.C. Trivedi, *High Perform. Polym.*, **4**, 151 (1992).
14. S.B. Shah, C.P. Patel and H.C. Trivedi, *Carbohydr. Polym.*, **26**, 61 (1995).
15. T. Tripathy and R.P. Singh, *Eur. Polym. J.*, **36**, 1471 (2000).
16. T. Tripathy, N.C. Karmakar and R.P. Singh, *J. Appl. Polym. Sci.*, **82**, 375 (2001).
17. Y. Cao, X. Qing, J. Sun, F. Zhou and S. Lin, *Eur. Polym. J.*, **38**, 1921 (2002).
18. T. Tripathy, N.C. Karmakar and R.P. Singh, *Int. J. Polym. Mater.*, **46**, 81 (2000).
19. V.D. Athawale and V. Lele, *Carbohydr. Polym.*, **41**, 407 (2000).
20. A.M.A. Nada and M.L. Hassan, *Polym. Degrad. Stab.*, **67**, 111 (2000).
21. F.R. Duke and A.A. Froist, *J. Am. Chem. Soc.*, **71**, 2790 (1949).
22. F.R. Duke and A.A. Froist, *J. Am. Chem. Soc.*, **73**, 5179 (1951).
23. T. Doba, C. Rodehed and B. Ranby, *Macromolecules*, **17**, 2512 (1984).
24. A.A. Berlin and V.N. Kislenco, *Prog. Polym. Sci.*, **17**, 765 (1992).
25. A. Pourjavadi and M.J. Zohuriaan-Mehr, *Starch/Starke*, **54**, 140 (2002).
26. L. Mr, S. Silong, W.M.Z.W. Yunus, Z.A. Rahman, M. Ahmad and M.J. Haron, *J. Appl. Polym. Sci.*, **77**, 784 (2000).
28. S.R. Shukla and G.V. Gopala, Rao, *J. Appl. Polym. Sci.*, **42**, 2163 (1991).