



Free Radical Graft Copolymerization of Acrylonitrile onto Sodium Hyaluronate Using Ammonium Persulfate

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The polysaccharide, sodium hyaluronate, was modified using ammonium persulfate-initiated graft copolymerization of acrylonitrile under inert atmosphere in a homogeneous aqueous medium. Grafting was confirmed using gravimetrically method and solubility test. The effect of various factors affecting on grafting, *i.e.* concentration of the initiator, monomer and polysaccharide as well as the reaction temperature were studied by conventional methods to achieve the optimum grafting parameters. According to the empirical rates of the polymerization and the graft copolymerization of acrylonitrile acid onto sodium hyaluronate backbone, the overall activation energy of the graft copolymerization reaction was estimated to be 13.4 kJ/mol.

Key Words: Sodium hyaluronate, Acrylonitrile, Graft copolymerization, Ammonium persulfate.

INTRODUCTION

Among the diverse approaches that are possible for modifying polysaccharides, grafting of synthetic polymer is a convenient method to add new properties to a polysaccharide with minimum loss of the initial properties of the substrate¹. Considerable interest has been focused on chemical modification by free radical graft copolymerization of hydrophilic and hydrophobic vinyl monomers biopolymers such as polysaccharides²⁻⁴. 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^{5,6}.

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. 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^{7,8}.

The chosen polysaccharide for modification is sodium hyaluronate. Sodium hyaluronate is a polysaccharide, which is distributed widely in the extracellular matrix of connective tissue in man. Sodium hyaluronate is today producing by biological culture of genetic transformed bacteria.

Of the monomers grafted, acrylonitrile has been the most frequently used one, mainly due to its highest grafting

efficiency^{9,10}, improving the thermal resistance of the graft copolymer¹¹ and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents^{2,9}.

The present report describes graft copolymerization of acrylonitrile onto sodium hyaluronate backbone, initiated by ammonium persulfate.

EXPERIMENTAL

Sodium hyaluronate and ammonium persulfate (APS) (all Fluka, Buchs, Switzerland) were used without further purification. Acrylonitrile (acetonitrile, from Merck) was used after vacuum distillation for removing inhibitor.

Grafting procedure: Graft copolymerization of acrylonitrile onto sodium hyaluronate was carried out with ammonium persulfate radical initiator under argon atmosphere. In a 100 mL flask, certain amount of sodium hyaluronate (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 (40-100 °C). A given amount of monomer, acrylonitrile (1.5-5.0 g), was added to the flask and the mixture was stirred for 15 min. Then, the initiator (0.02-0.50 g) was added to the mixture and continuously stirred for 120 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.

Homopolymer extraction: The graft copolymer was freed from polyacrylonitrile (PAN) homopolymer, by pouring 0.50 g of the product in 50 mL of dimethyl formamide solution.

The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer, the copolymer was filtered, washed with ethanol and dried in oven at 50 °C to reach a constant weight.

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 Fanta⁵. The percentage of grafting ratio (Gr %) stands for the weight percent of the graft copolymer synthetic part (PAA grafted) formed from initial sodium hyaluronate used.

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

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

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

The percentage of Add-on (Ad %) is the weight per cent of the grafted PAA of the graft copolymer.

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

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

$$\text{Homopolymer (Hp \%)} = 100 - \text{Grafting efficiency \%}$$

RESULTS AND DISCUSSION

Graft copolymerization mechanism: The mechanism of grafting acrylonitrile onto sodium hyaluronate using ammonium persulfate as a water soluble oxidizing initiator is shown in the **Scheme-I**. 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 acrylonitrile acid led to a graft copolymer.

Proof of grafting: Evidence of grafting was obtained by gravimetrically method as well as solubility characteristics of the products.

The existence of poly(acetonitrile) grafting was confirmed by the difference between solubility of the graft copolymer and the non-grafted homopolymer. Sodium hyaluronate and poly(acetonitrile) are soluble in water and DMF, respectively. When a reaction product was extracted with DMF and alter-

natively with water for 24 h, an insoluble solid still remained. A physical mixture of sodium hyaluronate and poly(acetonitrile) 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 sodium hyaluronate substrate and poly(acetonitrile) macromolecules.

The existence of poly(acetonitrile) grafting was also monitored gravimetrically. Increase in the mass of sodium hyaluronate, after extraction of homopolymer, was taken as evidence for grafting. This weight gain in sodium hyaluronate 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 acrylonitrile, sodium hyaluronate and ammonium persulfate as well as grafting temperature was studied in the light of grafting parameters.

Effect of polysaccharide concentration: Fig. 1 shows the relationship between sodium hyaluronate concentration and the grafting parameters. The increase in the sodium hyaluronate amount from 1 to 7 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.

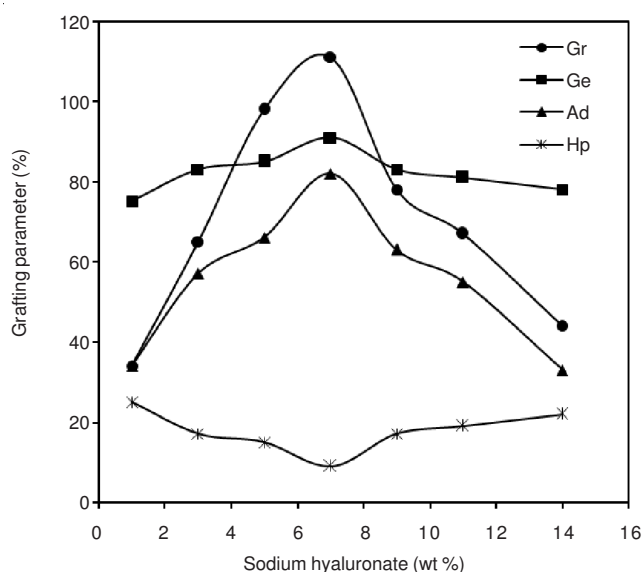
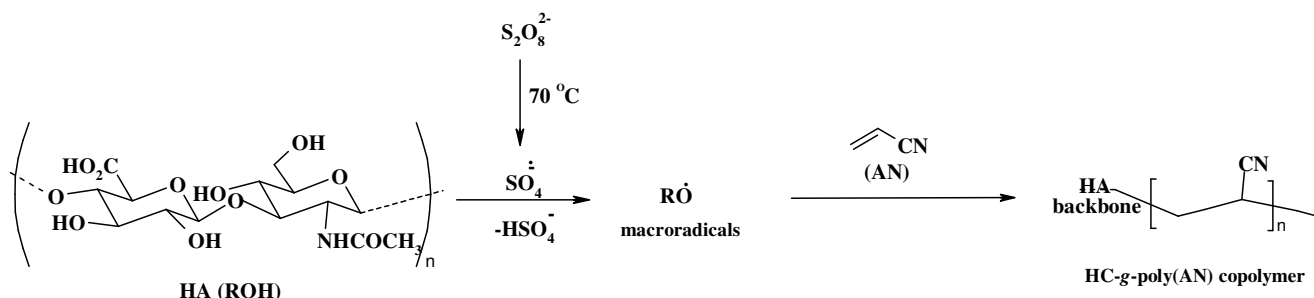


Fig. 1. Effect of polysaccharide concentration on the grafting parameters



Scheme-I: A brief proposed mechanism for ammonium persulfate-induced grafting of poly(acetonitrile) onto sodium hyaluronate

Effect of initiator concentration: Graft copolymerization was studied at various initiator concentrations by keeping other reaction conditions constant. As shown in Fig. 2, the grafting efficiency % and grafting ratio % increase with increasing in the initiator concentration and reach at a maximum value. Further increase of concentration of ammonium persulfate beyond 0.008 mol/L disfavoured the grafting parameters. A relatively high concentration of the initiator may cause a reduction of grafting efficiency % and grafting ratio % due to increase in the number of sodium hyaluronate free radicals terminated prior to AA addition. Furthermore, homopolymer formation at higher ammonium persulfate concentrations which compete with the grafting reaction for available monomer could lead to decrease in the grafting efficiency % and grafting ratio %.

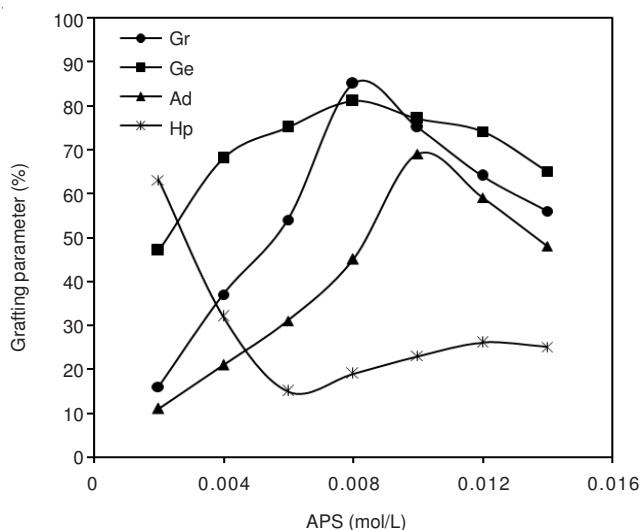


Fig. 2. Grafting parameters as functions of initiator concentration

Effect of monomer concentration: The effect of acrylonitrile concentration on the grafting parameters is presented in Fig. 3. In the initial stages, though both grafting efficiency % and grafting ratio % rise with increase in AA concentration, but beyond certain concentration of monomer, 0.8 mol/L, the grafting parameters decrease. The initial increase in grafting parameters could be associated with the greater availability of monomer molecules in the vicinity of sodium hyaluronate macroradicals. The decrease of grafting ratio % and grafting efficiency % with further increase in the acrylonitrile 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.

Effect of reaction temperature: Fig. 4 shows the influence of reaction temperature on grafting. An increase in temperature upto 60 °C increases the grafting parameters. This behaviour may be due to the higher rate of diffusion of acrylonitrile acid molecules to polysaccharide macroradicals. Moreover, higher temperatures increase the solubility of the reactants. On the other hands, since ammonium persulfate is a thermally dissociating initiator, it reacted very slowly at temperatures lower than its dissociation temperature 60 °C. The lower initiating

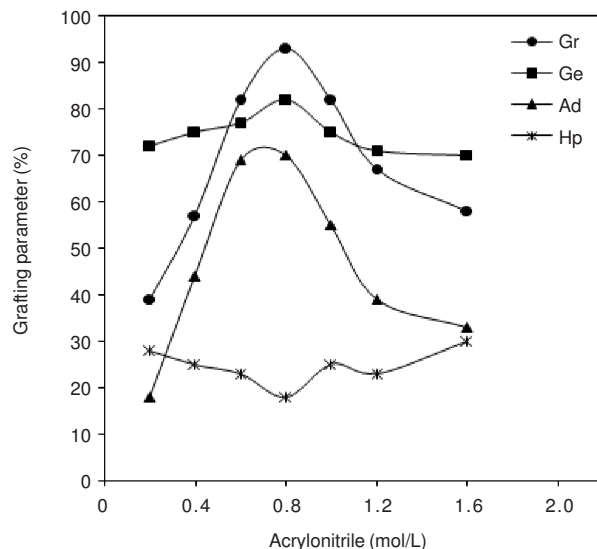


Fig. 3. Effect of the monomer concentration on the grafting parameters

radicals limited the extent of polymerization. The subsequent lower grafting can be explained on the basis of (a) oxidative degradation of polysaccharide chains by sulfate radical-anions and (b) increasing rate of termination and chain transfer reactions.

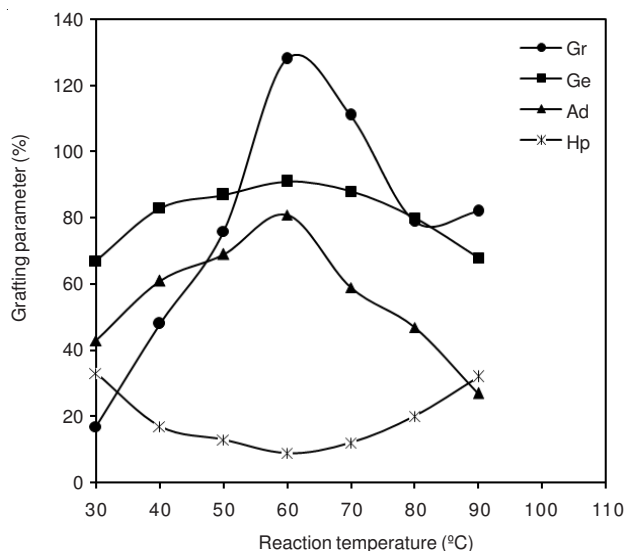


Fig. 4. Effect of the reaction temperature on the grafting parameters

Using the following empirical formula, the rate of graft copolymerization (R_g) was calculated:

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

The overall activation energy (E_a) of the graft polymerization reaction was calculated by using of the above equation and the slope of the plot $\ln R_g$ versus $1/T$ based on Arrhenius relationship [$k_p = A \exp(-E_a/RT)$]. Therefore, E_a for the graft copolymerization was found to be 13.4 kJ mol.

Conclusion

A novel modified polysaccharide was prepared using persulfate-initiated graft polymerization of acrylonitrile monomers onto sodium hyaluronate. In order to prove that

monomer molecules were grafted, solubility test and gravimetrically method were used. The synthetic conditions were systematically optimized through studying the influential factors including temperature, concentration of the initiator, monomers and sodium hyaluronate. The effect of the individual factors was investigated by calculating the grafting parameters, *i.e.*, grafting ratio (Gr), add-on(Ad) value and homopolymer content (Hp). The reaction conditions were attempted to optimize for obtaining graft copolymers with higher grafting parameters. Overall, the grafted polysaccharide may be a candidate for manufacture of moulded plastics, ion exchange resins and plastic films and in cosmetics. On the other hand, since non-biodegradable plastic waste is known as an ecological threat, such natural polymer-based plastics in fact, are the need of time. Hence, improving the thermal stability of the polysaccharides would make them better suited for, for instance, moulded articles.

REFERENCES

1. T. Heinze and T. Liebert, *Prog. Polym. Sci.*, **26**, 1689 (2001).
2. D.W. Jenkins and S.M. Hudson, *Chem. Rev.*, **101**, 3245 (2001).
3. J.M. Joshi and S.V. Kumar, *Polymer*, **47**, 2198 (2006).
4. T. Sun, P. Xu, Q. Liu, J. Xue and W. Xie, *Eur. Polym. J.*, **39**, 189 (2003).
5. G.F. Fanta, *Block and Graft Copolymerization*, Wiley, London (1973).
6. A. Hebeish and J.T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer-Verlag, Berlin (1981).
7. T. Tripathy and R.P. Singh, *Eur. Polym. J.*, **36**, 1471 (2000).
8. A. Pourjavadi, M.J. Zohuriaan-Mehr, A. Pooraghabarar and H. Hosseinzadeh, *J. Polym. Mater.*, **21**, 351 (2004).
9. G.F. Fanta and W.M. Doane, *Grafted Starches*. In *Modified Starches: Properties and Uses*; Wurzburg, O.B., Ed.; CRC Press: Boca Raton, Florida, pp. 149-178 (1986).
10. N.K. Sandle, O.P.S. Verma and I.K. Varma, *Thermochim. Acta*, **115**, 189 (1987).
11. V.D. Athawale and S.C. Rath, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C39**, 445 (1999).