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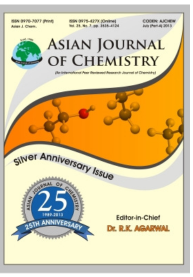

Effective Parameters onto Graft Copolymer Based on Carboxymethyl with Acrylic Monomer

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The effective parameters onto graft copolymer sodium carboxymethyl celloluse with acrylic monomers were performed. The graft copolymerization reaction was carried out in a homogeneous medium and by reaction of N-isopropylacrylamide (NIPAAm) and methacrylamide (MAAm) with carboxymethyl cellulose backbones. A mechanism for the graft copolymer formation was also suggested. Finally, the effect of ammonium persulfate, carboxymethyl cellulose concentration and MAAm/NIPAAm weight ratio and reaction temperature on the per cent grafting has been investigated.

Key Words: CMC, Grafting, Methacrylamide, N-Isopropylacrylamide.

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[5-7] and also development of selective permeable membranes[8], sorption agents[9] and in fabrication of drug delivery systems[10,11]. Grafting can be performed using free radical initiators, redox systems or photochemical process. Persulfate is a versatile oxidizing agent that through various redox reactions with many different organic substrates can create free radicals capable of initiating vinyl polymerizations[1]. Ammonium persulfate has been widely used by many investigators for initiating graft copolymerization of vinyl monomers onto various natural and synthetic polymers. The literature survey reveals that few of the modifications deal with chemical grafting of a pre-modified polysaccharide such as carboxymethyl cellulose. Ammonium persulfate-initiated grafting of vinyl monomers such as methyl acrylate, ethyl acrylate and ethyl methacrylate[7,8], AN/methyl methacrylate mixture[9], acrylamide (AAm)[10,11] and 4-vinylpyridine[12,13] onto CMC has been reported using different initiators, acrylic acid has also been photografted onto CMC. In addition, N-vinyl-2-pyrrolidone and its mixture with AA has been graft copolymerized onto mixtures of CMC/hydroxyethylcellulose to prepare cellulosic membrane with special biological effects. However, to the best of our knowledge, no report has been published on the optimization simultaneously of methacrylamide and N-isopropylacrylamide grafted onto CMC using APS-saccharide initiating system. As a part of our research program on polysaccharide modification, herewith we report the optimized APS-induced synthesis of CMC-*g*-poly(MAAm-*co*-NIPAAm) under an inert atmosphere.

EXPERIMENTAL

The polysaccharide, carboxymethylcellulose (CMC, degree of substitution 0.63, from Condinson Co., Denmark) was of analytical grade and was used as received. N-Isopropylacrylamide (NIPAAm, Merck) and methacrylamide (MAAm, Merck) were used as received. Ammonium persulfate (APS, Merck) was used without purification.

Graft polymerization: A general procedure was conducted as follows: carboxymethyl cellulose solution was prepared in a 1 L reactor equipped with mechanical stirrer and gas inlet. Carboxymethyl cellulose was dissolved in degassed distilled water. In general, 0.50 g of CMC was dissolved in 30 mL of distilled degassed water. The reactor was placed in a water bath preset at 60 ºC. Then 0.10 g of APS (dissolved in 5 mL water) as an initiator was added to CMC solution and was allowed to stir for 10 min at 60 ºC. After adding initiator, simultaneously variable amounts of MAAm and NIPAAm were added to the CMC solution. After 1 h, the reaction product was allowed to cool to ambient temperature and methanol (500 mL) was added to the product. After complete dewatering for 24 h, the product was filtered, washed with fresh methanol (2 × 50 mL) and dried at 50 ºC.

Homopolymer extraction: The graft copolymer, namely CMC-*g*-poly(MAAm-*co*-NIPAAm), was freed from polymethacrylamide and poly N-isopropylacrylamide homopolymers, by pouring 0.50 g of the product in 50 mL of DMF solution. The mixture was stirred gently at room temperature for 48 h. After complete removal of the homopolymer by centrifugating, the CMC-*g*-poly(MAAm-*co*-NIPAAm), was filtered, washed with methanol and dried in oven at 50 ºC to reach a constant weight[14].

Characteristic and determination of important-grafting parameters: The percentage of conversion (PC %), graft yield (Gr %) and graft efficiency (GE %) were evaluated with the following weight-basis expressions as reported by Fanta[12]:

From the increased weight, the percentage of conversion (PC %) can be estimated as the following equation:

$$\text{PC}\ (\%) = \frac{100(W_2 - W_0)}{W_1} \qquad (1)$$

where W_0, W_1 and W_2 designate the weight of CMC substrate, (MAAm + NIPAAm) monomers in feed and total weight product (copolymer and homopolymers), respectively. In this study, the value of W_1 was fixed at 1.0 g. The rough products were extracted by DMF in a centrifugating apparatus at least 48 h for the complete removal of the homopolymers. The graft yield (G %) and graft efficiency (GE %) are estimated as follows[12]:

$$\text{G}\ (\%) = \frac{100(W_3 - W_0)}{W_0} \qquad (2)$$

$$\text{GE}\ (\%) = \frac{100(W_3 - W_0)}{(W_2 - W_0)} \qquad (3)$$

or

$$\text{GE}\ (\%) = \frac{100(W_3 - W_0)}{(W_4 + W_3 - W_0)}$$

where W_3 and W_4 are the dried weight of grafted CMC after extraction and PMAAm + PNIPAAm homopolymers. Ethanol is a good solvent for PMAAm as well as a precipitant for pure CMC or grafted CMC, so the PMAAm + PNIPAAm homopolymers could be easily separated from the rough products. However, it seemed to be difficult to further separate the unreacted CMC from the products and the right separation methods are still in progress in my research. In view of the modification intention, the unreacted CMC is not very necessary to be separated from the products, so the blends of unreacted CMC and the graft copolymer CMC-*g*-poly(MAAm-*co*-PNIPAAm) were actually obtained in this research and their compositions were unknown. In several studies on the grafting modification of polymer, the unreacted substrate polymer and graft copolymer were also not separated from the products[15-18]. If the unreacted CMC could be separated from the products, the graft copolymer CMC-*g*-poly(MAAm-*co*-PNIPAAm) with higher G % could be obtained, but the values of PC % and GE % would not be affected.

RESULTS AND DISCUSSION

Optimization of the reaction conditions: In the present investigation, the effect of concentration of CMC, APS and MAAm/NIPAAm weight ratio, along with reaction temperature was studied, to optimize the reaction conditions. It may be found from the related curves that the trends of the "changes" are similar for grafting parameters Gr, GE and PC. The reason is the similar concepts applied for defining the grafting parameters (eqns. 1-3).

Effect of initiator concentration: For studying the initiator concentration effect on grafting parameters, amount of APS from 0.01-0.06 mol/L was varied (Fig. 1). The grafting ratio is increased with increasing the APS concentration from 0.01 up to 0.03 mol/L and then, it is decreased considerably with a further increase in the amount of APS. The maximum grafting ratio (352 %) is obtained at APS 0.03 mol/L. The number of active free radicals on the CMC backbone is increased in terms of the initiator levels lower than 0.03 mol/L. This accounts for the initial increment in grafting ratio up to a certain amount of APS. The grafting ratio decrease after the maximum may be attributed to increased number of produced radicals led to terminating step *via* bimolecular collision resulting in enhanced crosslink density[19].

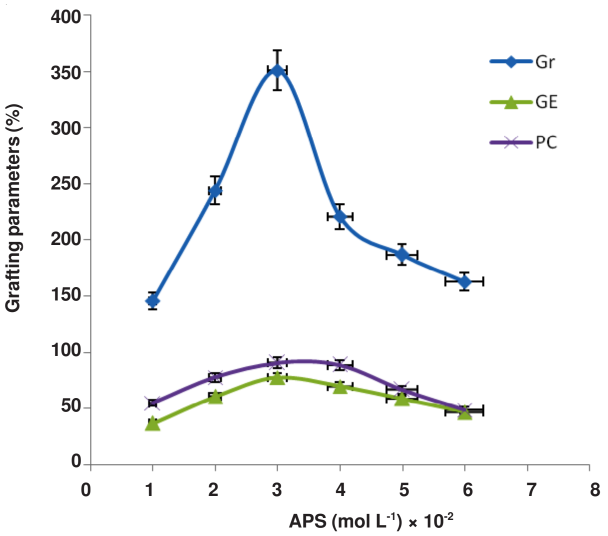


Fig. 1. Effect of initiator concentration on the grafting parameters. Reaction conditions: CMC 3 wt %, MAAm 1.50 mol L^{-1}, NIPAAm 0.50 mol L^{-1}, temperature 55 ºC, time 90 min

An additional reason for decreasing the grafting ratio can be related to decreasing molecular weight (MW) of the grafted PMAAm and PNIPAAm at high levels of APS concentration. Since MW inversely depends on initiator concentration, [I], higher [I] results in lower MW and, in turn, lower grafting ratio of the copoymer. On the other hand, free radical degradation of CMC substrate is also possible at high APS levels. A similar observation is recently reported by Chen and Zhao[20] in the case of degradation of chitosan with potassium persulfate. According to **Scheme-I**, the sulfate radical-anion produced from thermal dissociation of APS (step 1) abstracts a hydrogen atom from the acetal carbon of the CMC backbone (step 2). The resulting free radical intermediate is disconnected and lead to chain scissoring (step 3).

Effect of substrate concentration: The related to the grafting dependence on carboxymethylcelloluse (CMC) amount is showed in Fig. 2. Maximum grafting and the lowest homopolymers formation was observed at 1.25 g (5 wt %) CMC, while others reactants including, monomers, initiator and temperature were kept constant. Beyond this value, both grafting yield and graft efficiency values are considerably reduced. This behaviour is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher concentration of the substrate (from 1.0-5.0 wt % CMC). 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 graft efficiency 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.This observation is in close agreement with the results obtained by other investigators[19,20].

Effect of MAAm/NIPAAm weight ratio: The substrate CMC was treated with different weight ratio of MAAm/NIPAAm, is illustrated in Fig. 3. In this series reaction, the rest of variables was unchanged. The initial increase in percent graft could be originated from the greater availability of monomers molecules in the vicinity of the chain propagating sites of CMC macroradicals. In addition, higher MAAm/NIPAAm weight ratio enhances the hydrophilicity of the copolymer that, in turn, causes a stronger affinity for more per cent grafting. A further increase of monomers concentration, however, results in decreased Gr % and GE %. It is probably due to (a) preferential homopolymerization over graft copolymerization, (b) increase in viscosity of the medium which hinders the movement of free radicals and monomer molecules, (c) the enhanced chance of chain transfer to monomer molecules. The latter reason is in close agreement with similar starch-based hydrogels reported by Athawale and Lele[2].

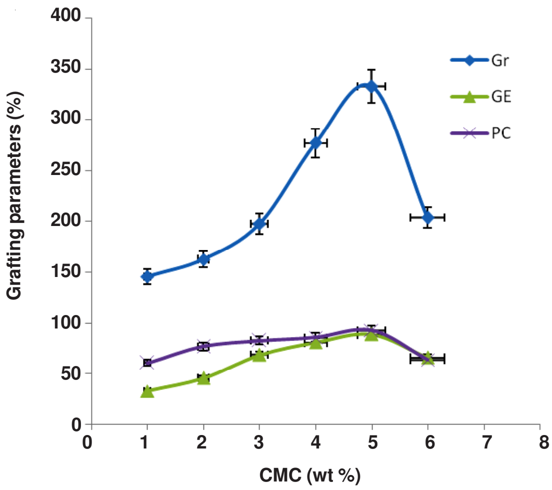


Fig. 2. Effect of polysaccharide concentration on the grafting parameters. Reaction conditions: APS 0.03 mol L^{-1}, MAAm 1.50 mol L^{-1}, NIPAAm 0.50 mol L^{-1}, temperature 55 ºC, time 90 min

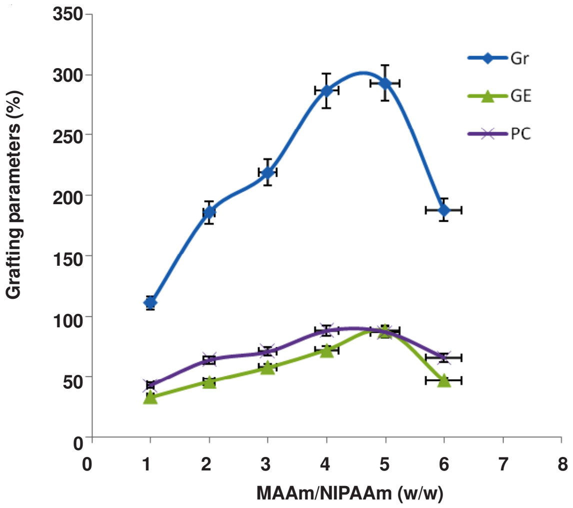
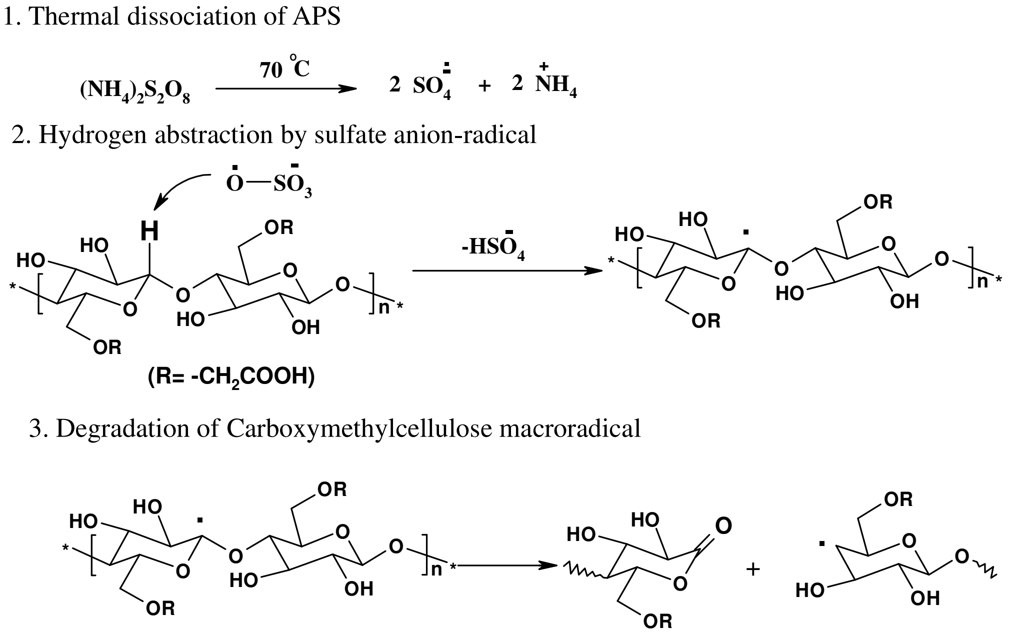


Fig. 3. Effect of monomers weight ratio on the grafting parameters. Reaction conditions: CMC 5 wt %, APS 0.03 mol L^{-1}, temperature 55 ºC, time 90 min



Scheme-I: A proposed mechanism for degradation of CMC substrate by the persulfate initiator

Effect of reaction temperature: The per cent graft of copolymer prepared with various reaction temperatures, is shown in Fig. 4. Higher temperatures favour the rate of diffusion of monomers to the CMC macroradicals as well as increase the kinetic energy of radical centers. In addition, higher temperatures increase the rate of decomposition of the thermally dissociating initiator, APS[20]. The temperatures higher than the optimum value (60 ºC), however, lead to low-graft copolymer. This percent-loss may be attributed to (a) oxidative degradation of CMC chains by sulfate radical-anions, (b) increasing the rate of termination and chain transfer reactions and (c) decomposition of APS to give O_2 (a radical scavenger), which reacts with primary free radicals (eqns. 3 and 4)[18], resulting in decreased molecular weight and decreased grafting (the sulfate radical anions may react with water to produce hydroxyl radicals (eqn. 4) and finally oxygen (eqn. 5)).

$$SO_4^{-\cdot} + H_2O \rightarrow HSO_4^{-} + HO^{\cdot} \tag{4}$$

$$2HO^{\cdot} \rightarrow H_2O_2 \rightarrow H_2O + 1/2O_2 \tag{5}$$

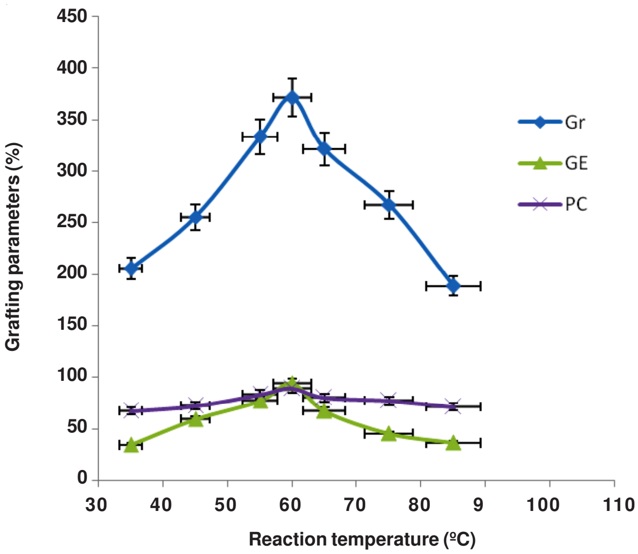


Fig. 4. Effect of reaction temperature on the grafting parameters. Reaction conditions: CMC 5 wt %, APS 0.03 mol L^{-1}, MAAm/NIPAAm 5, time 90 min

Conclusion

In synthesis of graft copolymer based on CMC polysaccharide, the main factors affecting the grafting parameters, including concentration of the initiator, monomers and CMC, reaction temperature was studied in detail. The optimum reaction conditions were found to be APS 0.03 mol/L, weight ratio of MAAm/NIPAAm = 5, CMC 5 % wt, reaction temperature 60 ºC. Under the optimized conditions the grafting parameters were calculated to be G % 371, GE % 94 and PC % 93 %. As an extension of this work, the CMC-*g*-poly(MAAm-*co*-NIPAAm) copolymer is being subjected to further modification to prepare thickeners and flocculants for aqueous systems.

REFERENCES

1. F.L. Buchholz and A.T. Graham, Modern Superabsorbent polymer Technology, Wiley, New York (1997).
2. V.D. Athawale and V. Lele, *Carbohydr. Polym.*, **35**, 21 (1998).
3. D. Castal, A. Ricard and R. Audebert, *J. Appl. Polym. Sci.*, **39**, 11 (1990).
4. P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York (1953).
5. L.H. Gan, G.R. Deen, Y.Y. Gan and K.C. Tam, *Eur. Polym. J.*, **37**, 1473 (2001).
6. S. Hua and A. Wang, *Carbohydr. Polym.*, **75**, 79 (2009).
7. J. Kost, Encyclopedia of Controlled Drug Delivery, Intelligent Drug Delivery Systems, Wiley, New York, Vol. 1 (1999).
8. W.F. Lee and W.Y. Yuan, *J. Appl. Polym. Sci.*, **77**, 1760 (2000).
9. G.R. Mahdavinia, A. Pourjavadi, H. Hosseinzadeh and M.J. Zohuriaan, *Eur. Polym. J.*, **40**, 1399 (2004).
10. N.A. Peppas and A.G. Mikes, Hydrogels in Medicine and Pharmacy, CRC Press, Boca Raton, Florida (1986).
11. L.B. Peppas and R.S. Harland, Absorbent Polymer Technology, Elsevier, Amsterdam 1990 (1994).
12. G.F. Fanta, In ed.: J.C. Salamone, in Polymeric Materials Encyclopedia, CRC Press: Boca Raton, FL, pp. 7901, 8051, Vol. 10 (1996).
13. R. Po, *J. Macromol. Sci-Rev. Macromol. Chem. Phys.*, **C34**, 607.
14. M.J. Zohuriaan-Mehr and A. Pourjavadi, *J. Polym. Mater.*, **20**, 113 (2003).
15. A. Pourjavadi, A.M. Harzandi and H. Hosseinzadeh, *Eur. Polym. J.*, **40**, 1363 (2004).
16. A. Pourjavadi and M. Kurdtabar, *Eur. Polym. J.*, **43**, 877 (2007).
17. G.V.N. Rathna and S. Damodaran, *J. Appl. Polym. Sci.*, **85**, 45 (2002).
18. A. Richter, A. Bund, M. Keller and K. Arndt, *Sens. Actuators B*, **99**, 579 (2004).
19. H. Yan, A. Saiani, J.E. Gough and A.F. Miller, *Biomacromolecules*, **7**, 2776 (2006).
20. J. Chen and Y. Zhao, *J. Appl. Polym. Sci.*, **75**, 808 (2000).