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Investigation effective parameters onto γ-radiation Graft Polymerization Acrylamide onto Carboxymethylcellulose

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ABSTRACT

The monomer, acrylamide, was graft copolymerized onto Carboxymethylcellulose (CMC) using γ-rays as initiator. The reactions were carried out in a homogenous aqueous medium. The results showed that the thermal stability of grafted polyacrylamide samples was remarkably improved. A plausible mechanism of grafting has also been suggested. The effect of various factors affecting on grafting, i.e. dose of δ-rays and concentration of the monomer and polysaccharide as well as the reaction temperature were studied by conventional methods to achieve the optimum grafting parameters.

Key words: Carboxymethyl Cellulose, Acrylamide, γ-radiation Graft Polymerization

Introduction

Graft copolymerization is an attractive means for modifying base polymers because grafting frequently results in the superposition of properties relating to the backbone and pendant chains. Considerable interest has been focused on chemical modification by free radical graft copolymerization of hydrophilic and hydrophobic vinyl monomers biopolymers such as polysaccharides [1-4]. 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 [5-9].

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 [10].

Radiation grafting technology is well established and accepted by industry. Radiation polymerization, radiation crosslinking and controlled degradation of polymers comprise most of commercial applications of radiation technology [11-12].

The chosen polysaccharide for modification, i.e. Carboxymethylcellulose (CMC), is the most well-known and most important type of polysaccharide. Carboxymethylcellulose sodium salt (CMC) is the first water soluble ionic derivative of cellulose prepared in 1918 and produced commercially in the early 1920's in Germany. It has been the most important ionic cellulose ether with a worldwide annual production of 300,000 tons. It is widely used in pharmaceuticals, detergents, cosmetics, foods, paper and textile industries due to its viscosity-increasing and emulsifying properties. However, it may need to be further modified for some special applications.

Of the monomers grafted, acrylamide has been the most frequently used one, mainly due to its highest grafting efficiency [13], improving the thermal resistance of the graft copolymer [14], and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents [15].

Results and Discussion

Graft copolymerization mechanism:

The mechanism of grafting acrylamide onto carboxymethylcellulose (CMC) using γ-rays as an initiator is shown in the Scheme 1. It should be mentioned that during the irradiation of AAm, CMC and water ternary mixture, most of the energy is absorbed by water and only a very small fraction by other components. Thus, the initiation occurs mainly by an indirect effect. Hydroxyl radicals, formed during irradiation, add to one side of the AAm

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double bond and leads to the formation of an unpaired spin on the other side of the vinyl bond. In this way, homo polymerization of AAm is initiated. Attack of OH radicals on CMC would lead almost solely to the break age of C–H bonds. This fact is very well known from radiation chemistry of alcohols and carbohydrates in aqueous solution. A much more probable pathway is the addition of a AAm molecule (not a radical) to the CMC-based radical, followed by polymerization leading to the growth of a branched chain.

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 (Fanta1986) . The percentage of grafting ratio (Gr%) stands for the weight percent of the graft copolymer synthetic part (PAN grafted) formed from initial sodium hyaluronate used.

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

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

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

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

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

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

$$Homopolymer(\%Hp) = 100 - \%Ge$$

Optimization of the reaction conditions:

In the present investigation, the effect of concentration of CMC, δ-rays and AAm, along with reaction time 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 Gr, Ge, and Ad. The reason is the similar concepts applied for defining the grafting parameters (Eqs. 1-4).

Effect of CMC concentration:

The effect of CMC concentration on graft copolymerization was depicted in Figure 1. With increasing the CMC amount, more reactive grafting sites are formed which is favorable for grafting. This can account for initial increment in grafting parameters up to 0.8 %W/V of CMC 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 [17-19].

Effect of δ-rays dose:

Graft copolymerization was studied at various doses of δ-rays by keeping other reaction conditions constant. As shown in Figure 2, the %Ge and %Gr increase with increasing in the doses of δ-rays and reach at a maximum value. Further increase of doses of δ-rays beyond 25 kGy disfavoured the grafting parameters. A relatively high dose of δ-rays may cause a reduction of %Ge and %Gr due to increase in the number of CMC free radicals terminated prior to AN addition. Furthermore, homopolymer formation at higher doses of δ-rays which compete with the grafting reaction for available monomer could lead to decrease in the %Ge and %Gr.

Effect of monomer concentration:

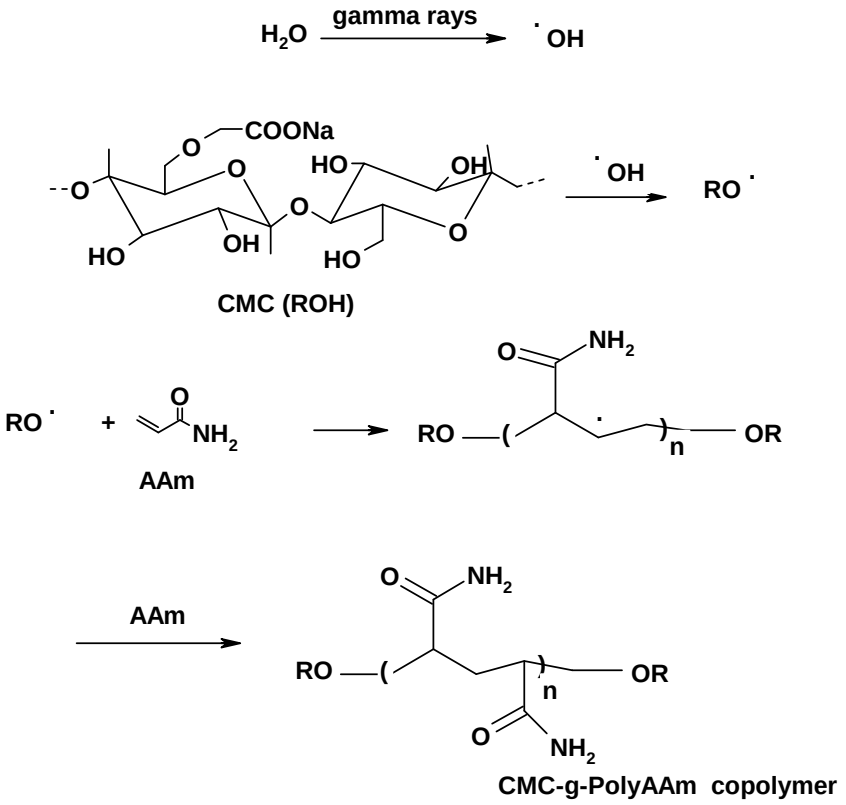
The effect of AAm concentration on the grafting parameters is presented in Figure 3. In the initial stages, though both %Ge and %Gr rise with increase in AN concentration, but beyond certain concentration of monomer, 0.6 mol/L, the grafting parameters decrease. The initial increase in grafting parameters could be associated with the greater availability of monomer molecules in the vicinity of CMC macroradicals. The decrease of %Gr and %Ge with further increase in the AN concentration may be explained as follows [19]: (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 [21].

Effect of reaction time:

Figure 4 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 CMC

surface, may be other possible reasons for the diminished grafting at longer reaction times. Similar time dependency of grafting parameters was reported by others [18].

It should be pointed out that, as shown in the figures 6-10, the magnitudes of changes of Gr and Ge differ drastically, i.e. the changes of Gr is much more than Ge 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 Gr much more than on Ge. In other word, the parameter Gr is more sensitive to the initial reactants than Ge.



Scheme 1: A brief proposed mechanism for γ-rays -induced grafting of acrylamide onto CMC.

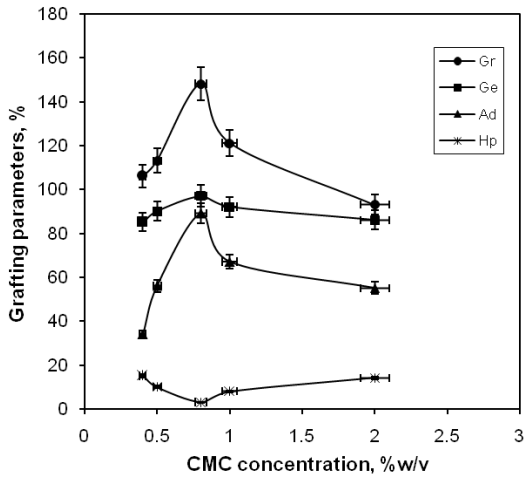


Fig. 1: Effect of carboxymethylcellulose concentration on the grafting parameters.

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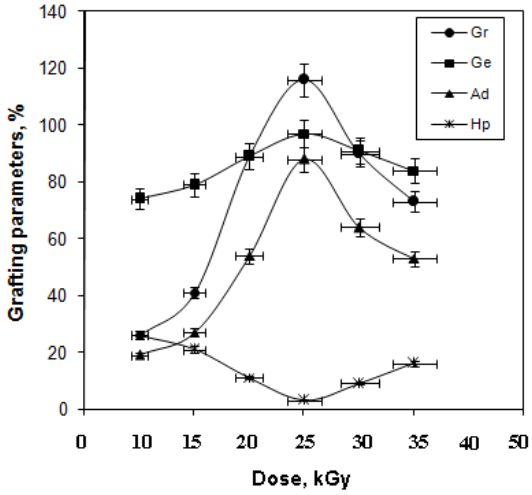

Fig. 2: Effect of initiator doses on the grafting parameters.

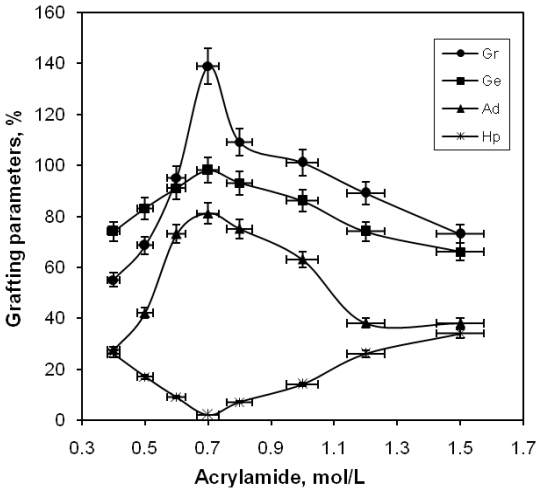

Fig. 3: Effect of Acrylonitrile concentration on the grafting parameters.

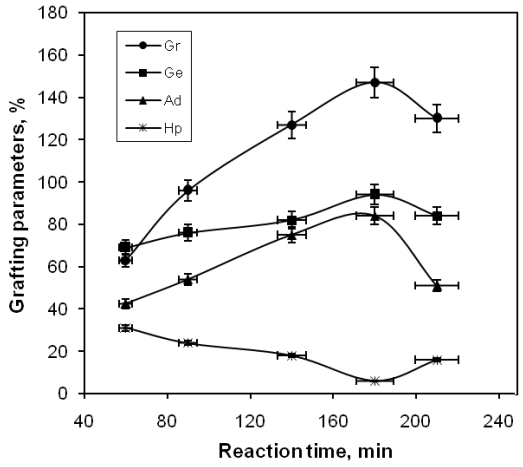

Fig. 4: Effect of reaction time on the grafting parameters.

Conclusion:

After synthesis of graft copolymer based on Carboxymethylcellulose-g-polyacrylamide, using δ-rays as efficient free radical initiators, we optimized The synthetic conditions systematically through studying the influential factors including, doses of δ-rays as well as concentration of the monomers and polysaccharide. Under the optimized conditions the grafting parameters were calculated to be Gr 115 %, Ge 97 %, Ad 75 %, and Hp 3 %. As an extension of this work, the CMC-g-PMAN copolymer is being subjected to further modification to prepare thickeners and flocculants for aqueous systems.

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