

Studies on Synthesis of Amphoteric Cellulosic Graft Copolymers*

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Abstract A series of amphoteric cellulosic graft copolymers, containing anionic carboxymethyl and cationic quaternary ammonium groups, were prepared by the graft copolymerization of carboxymethylcellulose (CMC) with dimethyldiallylammonium chloride (DMDAAC) using potassium permanganate / sulphuric acid initiation system under different conditions. Major factors affecting the polymerization reaction, such as the degree of substitution (DS) of CMC, the amount of DMDAAC, acid concentration and the amount of initiator, were studied, and the mechanism for grafting of DMDAAC onto CMC using the $KMnO_4/H_2SO_4$ redox system was elucidated.

Keywords amphoteric cellulosic graft copolymers, carboxymethylcellulose, dimethyldiallylammonium chloride, graft copolymerization

Classification number O 631.51

Amphoteric polymers have unique physicochemical characteristics owing to the presence of both anionic and cationic groups^[1]. Their applications have been reported as oil-field additives^[2], flocculants^[3], polymeric catalysts^[4], and carriers to prolong the action of drugs^[5], membranes^[6], and so on. Usually, these polymers are made of synthetic polyelectrolytes. Due to environmental issues, growing efforts have been forward in developing modified natural polymers with amphoteric ions, which may guarantee biodegradability^[7]. In this work, a series of amphoteric cellulosic graft copolymers, containing anionic carboxymethyl and cationic quaternary ammonium groups, were prepared by the graft copolymerization of carboxymethylcellulose (CMC) with dimethyldiallylammonium chloride (DMDAAC) using potassium permanganate / sulphuric acid initiation system under different conditions.

1 Experimental

1.1 Materials

CMCs with different degree of substitution (DS, the number of carboxymethyl groups in one glucopyranose unit) were purchased from Guangzhou Hongguang Chemical Factory, their DS was determined by conductometric titration^[8]. DMDAAC was supplied by Guangzhou Fine Chemical Industry Company. Potassium permanganate and sulphuric acid

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were of laboratory grade.

1.2 Graft copolymerization procedure

The graft polymerization reaction was carried out as follows. The CMC sample treated with KMnO_4 solution was introduced into a reaction flask, to which a solution consisting of a specific concentration of H_2SO_4 and DMDAAC was placed. The reaction mixture was kept in 100 mL and was stirred for 4 h at 60°C under nitrogen. After the copolymerization, the graft copolymers was separated with ethyl alcohol and dried at 40°C under vacuum.

1.3 Characterization by grafting parameters and IR spectroscopy

The graft copolymers were characterized by the following parameters (grafting percentage, Y_G ; grafting efficiency, E_G):

$$Y_G = \frac{m(\text{graft product}) - m(\text{CMC})}{m(\text{CMC})} \times 100\%$$

$$E_G = \frac{m(\text{graft product}) - m(\text{CMC})}{m(\text{DMDAAC})} \times 100\%$$

The IR spectra of the ungrafted CMC and the graft copolymer were run on RFX-65 Spectrophotometer using KBr pellets in range of $400 \sim 4\,000 \text{ cm}^{-1}$.

2 Results and discussion

2.1 Mechanism for grafting

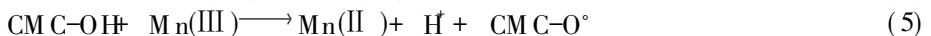
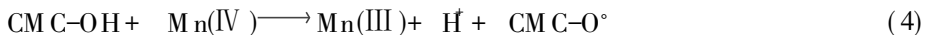
$\text{KMnO}_4/\text{H}_2\text{SO}_4$ redox system was used as the initiator due mainly to its high selectivity and effectiveness. The self-polymerization of DMDAAC under the conditions similar to the graft copolymerization has been carried out and no homopolymer was found.

When CMC sample is treated with KMnO_4 solution, it turns into either brown or dark brownish colour. This colour is due to the deposition of MnO_2 . The amount of MnO_2 depends on the concentration of KMnO_4 solution used.

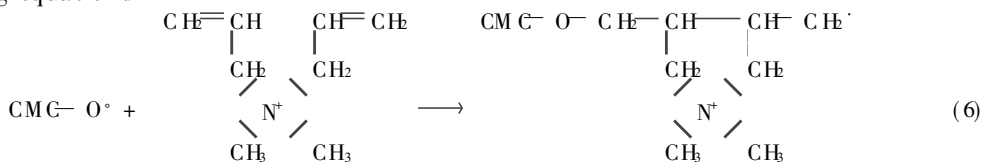
As suggested by Hebeish et al^[9], $\text{KMnO}_4/\text{H}_2\text{SO}_4$ redox system may create free radicals as follows:

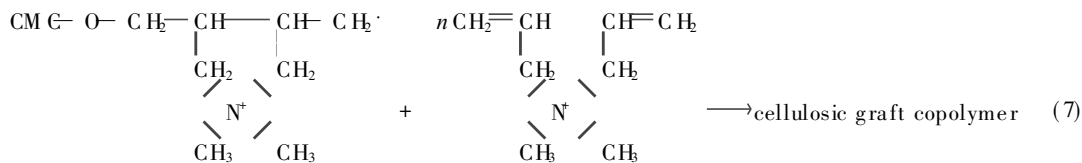


Once the radical, HSO_4^\cdot , or the hydroxyl radical, HO^\cdot , attacks CMC, forming a cellulosic macro-radical. The latter may also be formed according to the following reaction



In presence of DMDAAC the system will yield cellulosic graft copolymer as shown by following equations





The presence of CMC-g-DMDAAC copolymer in above reactions has been verified by IR spectra shown in Fig. 1. Compared with the spectrum of CMC sample (Fig. 1A, DS= 0.73), the spectrum of the CMC-g-DMDAAC copolymer (Fig. 1B, DS= 0.73, $Y_G = 113.3\%$, $E_G = 46.4\%$) shows not only the characteristic bands of cellulosic substrate at 1618 and 3444 cm^{-1} [10], but also the characteristic bands of C-N group at 1323 cm^{-1} and 953 cm^{-1} [11].

2.2 Factors affecting polymerization

(1) Effect of DS of CMC. Fig. 2 shows the effect of DS of CMC on the graft copolymerization of CMC with DMDAAC. It is seen that both the Y_G and E_G increase significantly with increasing of DS from 0.44 to 0.73 then decrease significantly with DS up to 0.86. It seems that the introduction of -CH₂COOH groups in the cellulose molecules causes two opposite effects

(a) opening up the cellulose structure thereby enhancing the diffusion and adsorption of both monomer and initiator, resulting in increase of Y_G and E_G up

(b) blocking some of the hydroxyl groups along the cellulose chains, resulting in decrease Y_G and E_G . It is likely that effect (a) predominates up to a DS of 0.73, and after that effect (b) becomes much more pronounced.

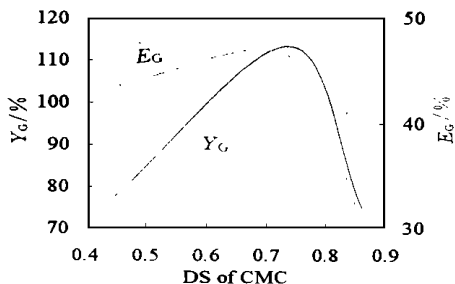


Fig. 2 Effect of DS of CMC on grafting
 $m(\text{CMC}) = 3.00 \text{ g}$, $m(\text{DMDAAC}) = 7.32 \text{ g}$
 $m(\text{KMnO}_4) = 0.34 \text{ g}$; $c(\text{H}_2\text{SO}_4) = 1.8 \text{ mol/L}$,
 6.0 mol/L ; $V(\text{reaction medium}) = 100 \text{ mL}$

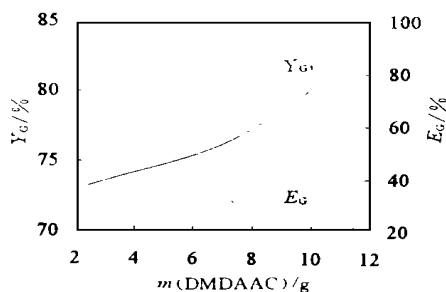
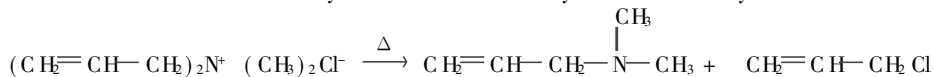


Fig. 3 Effect of DMDAAC amount on grafting
 $m(\text{CMC}) = 3.00 \text{ g}$ (DS= 0.73); $m(\text{KMnO}_4) = 0.34 \text{ g}$;
 $c(\text{H}_2\text{SO}_4) = 1.8 \text{ mol/L}$, 3.0 mol/L ;
 $V(\text{reaction medium}) = 100 \text{ mL}$ Y_G E_G

(2) Effect of DMDAAC amount. Fig. 3 shows the effect of DMDAAC amount on the graft copolymerization of CMC with DMDAAC. Obviously, the Y_G increases greatly

by increasing the amount of DMDAAC, and the opposite holds true for the Y_G . Enhancement in Y_G at high DMDAAC concentration could be associated with greater availability of monomer molecules in the vicinity of CMC molecules as well as in the polymerization medium, which would favour greater opportunity for DMDAAC to react with CMC via grafting. On the other hand, the decrease in E_G may be due to higher rates of thermal decomposition of DMDAAC into allyl chloride with very low reactivity^[12]:



Hence, besides enhancing the grafting, increasing DMDAAC concentration increases the probability of allyl chloride formation.

(3) Effect of KMnO_4 amount. Fig. 4 reveals the effect of KMnO_4 amount on the graft copolymerization of CMC with DMDAAC. It is noticed that increasing the amount of initiator from 0.17~ 0.26 g causes an increase in Y_G and E_G , and further increase to 0.34 g causes a decrease in Y_G and E_G . This behavior may be interpreted as the comprehensive result of two competing reactions, i. e. The effect of Mn(IV) on the generation of active sites on the CMC macromolecules and the oxidative termination of the growing chains. In addition, the decrease of the Y_G and E_G may also be attributed to a lower diffusion rate of DMDAAC from the aqueous phase to the CMC phase owing to the excess amount of MnO_2 deposited.

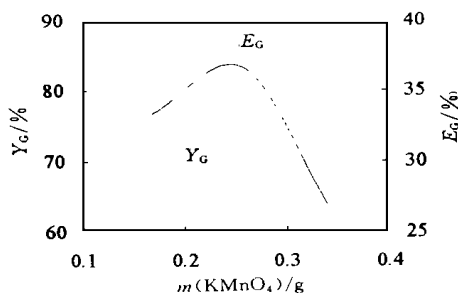


Fig. 4 Effect of KMnO_4 amount on grafting
 $m(\text{CMC}) = 3.00 \text{ g}$ ($\text{DS} \approx 0.73$)
 $m(\text{DMDAAC}) = 7.32 \text{ g}$; $c(\text{H}_2\text{SO}_4) = 1.8 \text{ mol/L}$,
 6.0 mL ; $V(\text{reaction medium}) = 100 \text{ mL}$

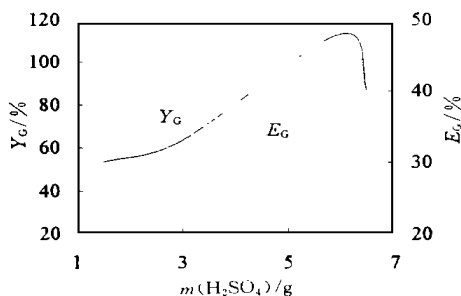


Fig. 5 Effect of H_2SO_4 amount on grafting
 $m(\text{CMC}) = 3.00 \text{ g}$ ($\text{DS} \approx 0.73$);
 $m(\text{DMDAAC}) = 7.32 \text{ g}$; $m(\text{KMnO}_4) = 0.34 \text{ g}$;
 $V(\text{reaction medium}) = 100 \text{ mL}$

(4) Effect of acid amount. Fig. 5 shows the effect of H_2SO_4 amount on the graft copolymerization of CMC with DMDAAC. It is evident in Fig. 5, that the Y_G and E_G increases with increasing the acid amount, reaching a maximum, and then falling at higher concentration. The increase in the Y_G and E_G may be attributed to that suitable acid concentration would be favorable to the above reaction equations (1), (5)~ (7). The fall in the Y_G and E_G at higher acid concentration could be attributed to the following reasons:

(a) The side reactions such as



increases at higher acid concentration. Thus, besides consuming some MnO_2 (required for production of initiating species), this leads to constant production of inhibiting oxygen^[13].

(b) The initiating species may be destroyed by side reactions, for instance, reaction of

the acid radicals with Mn(III).

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两性纤维素接枝共聚物的合成研究

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摘要 采用 $\text{KMnO}_4/\text{H}_2\text{SO}_4$ 氧化还原引发体系, 首次将羧甲基纤维素 (CMC) 与二甲基二烯丙基氯化铵 (DMAAC) 进行接枝聚合, 制备了一系列分子中同时含有阴离子羧甲基和阳离子季铵基团的两性纤维素接枝共聚物. 研究了 CMC 取代度、DMAAC 加量、 KMnO_4 用量和 H_2SO_4 浓度对接枝共聚的影响, 并对其聚合反应机理作了探讨.

关键词 两性纤维素接枝共聚物, 羧甲基纤维素, 二甲基二烯丙基氯化铵, 接枝聚合

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