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Key Words: Amphoteric Cellulosic Copolymers, Carboxymethylcellulose, Trimethylallylammonium Chloride, Graft Copolymerization, Clay-Hydration Suppressant

ABSTRACT

Graft copolymerization of cationic monomer trimethylallylammonium chloride onto anionic carboxymethylcellulose has been investigated in aqueous medium using potassium permanganate/sulphuric acid redox system as initiator, involving the identification of grafting, the mechanism for grafting and various factors affecting grafting. The prepared cellulosic copolymers with amphoteric functional groups have been found to be effective to retard the hydration of clay minerals, showing a potential use as new clay-hydration suppressant for oilfields.

INTRODUCTION

In recent years, chemical modification of carboxymethylcellulose (CMC) by grafting hydrophilic vinyl monomers with nonionic or anionic func-

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tional groups, such as acrylamide, acrylonitrile and acrylic acid, has gained considerable attention and proved of value in preparing new polymeric materials with special properties and enlarging the range of its utilization [1-4]. However, grafting hydrophilic vinyl monomers with cationic functional groups onto CMC has been scarcely studied. In this work, the graft copolymerization of cationic monomer trimethylallylammonium chloride (TMAAC) onto CMC was investigated in aqueous medium using $\text{KMnO}_4/\text{H}_2\text{SO}_4$ redox system as initiator, and the work was further extended to explore the possibility of the prepared poly (TMAAC)-CMC graft copolymers as new clay-hydration suppressant for oilfield.

EXPERIMENTAL

Materials

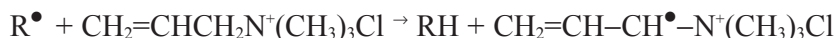
CMC was purchased from Guangzhou Hongguang Chemical Factory, its degree of substitution (the number of carboxymethyl groups in one glucopyranose unit) is 0.73. Cationic monomer TMAAC was prepared from the reaction of allyl chloride with trimethylamine according to the literature [5]. Potassium permanganate and sulphuric acid were of laboratory grade. Clay, containing 96 wt% calcium montmorillonite, was kindly provided by the China National Oil & Gas Exploration & Development Corporation.

Grafting and Homopolymerization of TMAAC

The graft-copolymerization reaction was carried out in a 250-mL four-necked, round-bottomed flask equipped with stirrer, thermometer, reflux condenser, and gas inlet tubes. In a typical grafting experiment, an exact amount of dry CMC was first dissolved in a specific concentration of KMnO_4 solution, followed by adding the determined quantities of H_2SO_4 and TMAAC in this order. Then, the flask content was stirred in a thermostatic water bath at 60°C for 4 hours. Nitrogen gas was purged into the reaction mixture to avoid the presence of oxygen. As the grafting proceeds, the grafting system becomes homogeneous. After the copolymerization, the graft sample was separated by precipitation using acetone as a non-solvent and extracted with aqueous isopropanol, and then dried at 35°C under vacuum to constant weight. In all cases, no detectable amount of the homopolymer was separated.

In order to confirm the absence of the homopolymer and explore the grafting mechanism, the homopolymerization of TMAAC was conducted with

all other usual procedure and reaction conditions, except that CMC was not added to the reaction mixture deliberately. As expected, no homopolymer was found, suggesting the reaction did not take place. This may be attributed to the transfer reaction between the free radicals (R^\bullet), which initiate the polymerization, and the monomer molecules [6]:



Grafting parameters such as the grafting percentage (GP) and grafting efficiency (GE) were determined as follows:

$$GP(\%) = \frac{W_2 W_1}{W_1} \times 100 \quad GE(\%) = \frac{W_2 W_1}{W_3} \times 100$$

where W_1 , W_2 , and W_3 denote the weight of initial CMC, grafted CMC and TMAAC, respectively.

IR and Viscosity Measurements

The existence of grafting was confirmed by observing the difference between the spectra of ungrafted CMC and that of grafted CMC and the viscosity behavior of ungrafted CMC and grafted CMC solution in different PH conditions. The IR spectra were run on RFX-65 Spectrophotometer using KBr pellets in the range of $400-4000 \text{ cm}^{-1}$. The reduced viscosity was measured at $30.00 \pm 0.05^\circ\text{C}$ using a Ubbelohde viscometer.

Clay-Hydration Test

40 g clay, already dried at 120°C for 6 hours, was pressed into a piece under 5MPa pressure for 5 minutes and then was fixed in the WZ-2 type swelling apparatus (Nanjing Soil Apparatus Factory, China). The linear expansion of the clay was recorded for the duration of the test after the clay had contacted various sample fluids.

RESULTS AND DISCUSSION

Identification of Grafting

Figure 1 shows the IR spectra of CMC and grafted CMC. Compared with the spectrum of CMC, the spectrum of grafted CMC shows not only the

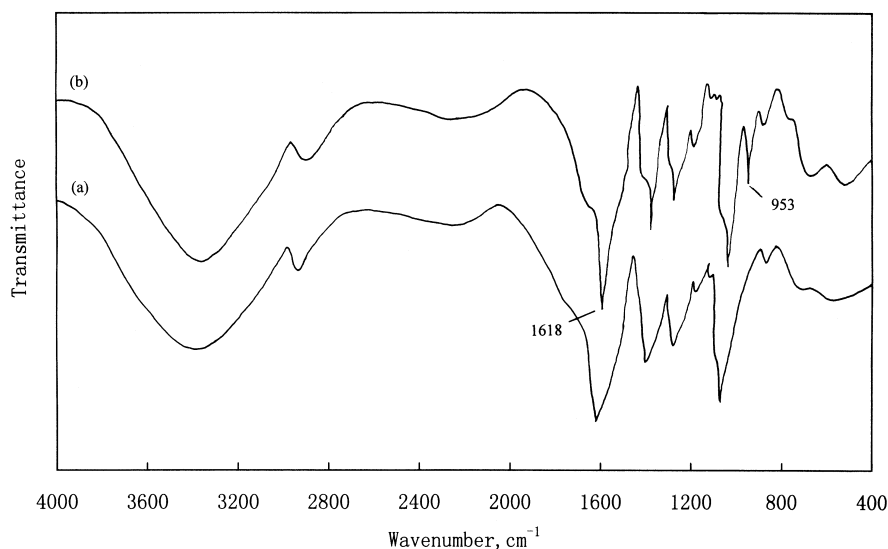


Figure 1. IR spectra of (a) CMC and (b) grafted CMC (GP=33%).

characteristic bands of carboxylic groups in CMC at 1618 cm^{-1} [7], but also the additional band at 953 cm^{-1} , which is attributed to the stretching vibration of $-\text{CH}_2-$ bonded with quaternary ammonium groups in poly(TMAAC) chains [8]. Figure 2 shows the reduced viscosity versus pH curves of CMC and grafted CMC dissolved in 0.20 M NaCl . Different from CMC, grafted CMC has an isoelectric point characteristic of amphoteric polymers in solution [9]. Namely, the positive charges from TMAAC units and the negative charges from anionic carboxymethyl substituents in CMC become almost equal at this pH within a grafted CMC polymer chain. These indicate that TMAAC has been grafted into CMC and the grafted CMC has amphoteric structure.

Mechanism for Grafting

From the above-mentioned experiments, it is known that the presence of the polysaccharide (CMC) is essential for the creation of free radical sites, which further initiated the process of graft copolymerization. Thus, it may be inferred that the grafting reaction initiated by $\text{KMnO}_4/\text{H}_2\text{SO}_4$ redox system is characterized by first producing free radicals on the CMC macromolecular backbone and then adding TMAAC molecules to form CMC macro-radicals.

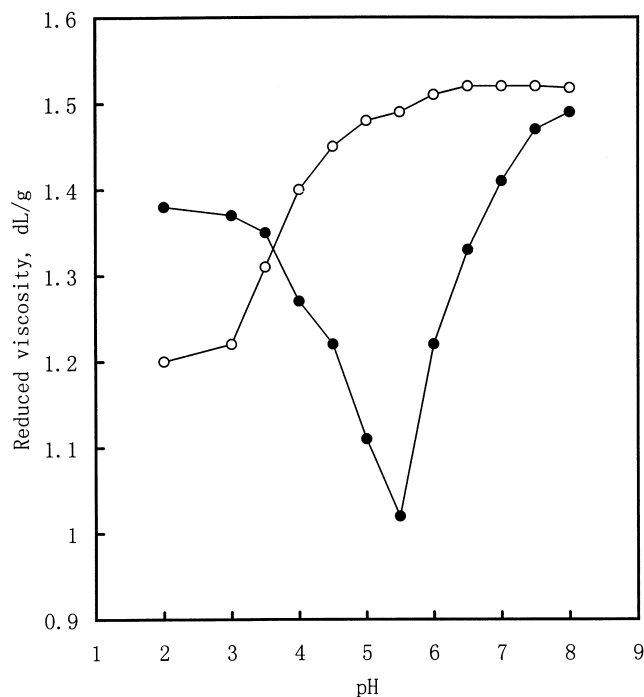


Figure 2. Reduced viscosities of CMC (○) and grafted CMC (●, GP=33%) in 0.20M NaCl at different pH. Polymer concentration = 0.10g/dL.

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

According to Hebeish *et al.* [10], $\text{KMnO}_4/\text{H}_2\text{SO}_4$ redox system may create free radicals as follows:



Once the radical HSO_4^\bullet or the hydroxyl radical HO^\bullet (R^\bullet) attacks CMC, the CMC macro-radicals are formed as suggested by the following equation:

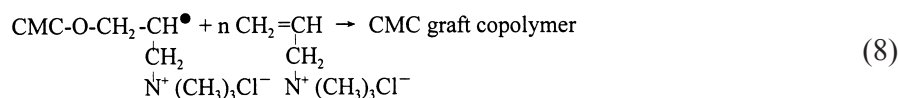
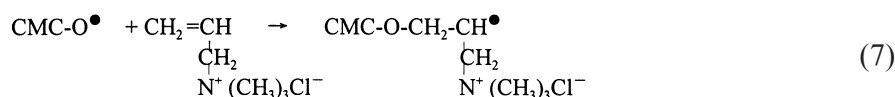


The CMC macro-radicals may also be formed according to the following reaction:



Since no homopolymer is formed, the CMC macro-radicals may preferentially formed according to Equations 5 and 6 compared to the hydrogen-abstracting reaction by HSO_4^\bullet and/or HO^\bullet radicals (Equations 1-3).

In the presence of TMAAC, the system will yield CMC graft copolymer as shown by following equations:



Finally, termination of the growing grafted chain may occur via the reaction with the initiator, disproportion, coupling, or chain transfer.

Factors Affecting Grafting

Figure 3 shows the effect of initiator concentration on the grafting. It is noticed that increasing KMnO_4 concentration up to $0.020M$ causes an increment in the GP and GE, and further increase causes a decrease in the GP and GE. This behavior may be interpreted as the comprehensive result of two competing reactions, i.e. the action of Mn^{IV} on the generation of active sites on the CMC macromolecules and the oxidative termination of the growing chains.

Figure 4 shows the effect of H_2SO_4 amount on the grafting. Obviously, the GP and GE increase with increasing the acid amount, attains a maximum, and then falls at higher concentration. The increase in the GP and GE may be attributed to that suitable acid concentration would be favorable to the above reaction Equations 1, 6, 7, and 8. The fall in the GP and GE at higher acid concentration could be attributed to the following reasons [11]:

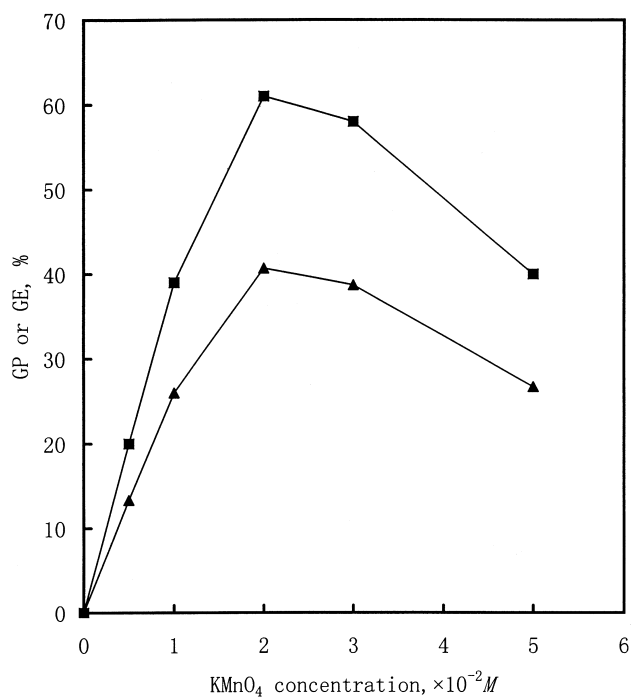


Figure 3. Effect of KMnO_4 concentration on the grafting: (■) GP; (▲) GE. Conditions: CMC, 2.0 g / dL; TMAAC, 3.0 g / dL; H_2SO_4 , 0.25 N.

(a) The side reactions such as



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

(b) The initiating species may be destroyed by some side reactions, for instance, the reaction of the acid radicals with Mn^{III} .

Figure 5 shows the effect of TMAAC amount on the grafting. It is clear that the GP increases greatly by increasing the amount of TMAAC and the opposite holds true for the GE. Enhancement in GP at high TMAAC 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 favor greater opportunity for TMAAC to react with CMC via grafting.

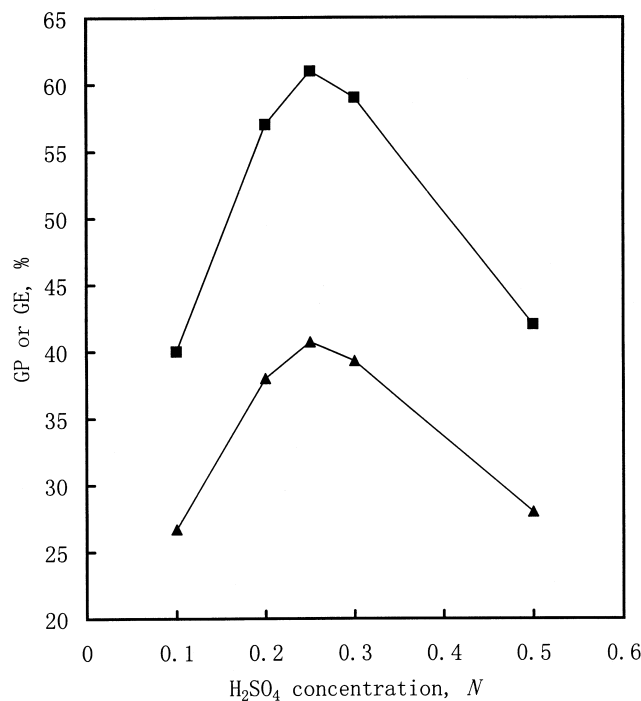


Figure 4. Effect of H₂SO₄ concentration on the grafting: (■) GP; (▲) GE. Conditions: CMC, 2.0 g / dL; TMAAC, 3.0 g / dL; KMnO₄, 0.20 × 10⁻² M.

Figure 6 shows the effect of CMC amount on the grafting. It is seen that both the GP and GE increase with increasing CMC concentration from 0.5 to 2.0 g/dL and then have a decrease with further increasing CMC concentration. It appears that the introduction of CMC causes two opposite effects:

- (a) producing the CMC macro-radicals, resulting in GP and GE up;
- (b) increasing the viscosity of reaction medium thereby affecting the diffusion of both monomer and initiator, resulting in GP and GE down.

It is likely that effect (a) predominates up to 2.0 g/dL of CMC after which effect (b) becomes much more pronounced.

Suppression of Clay Hydration

The hydration of clay containing formations has always been a major problem when drilling oil and gas wells for oilfields. To retard the hydration of clay minerals, amphoteric synthetic polymers have been used and found to be more effective than conventional anionic polymers or cationic polymers [12-15].

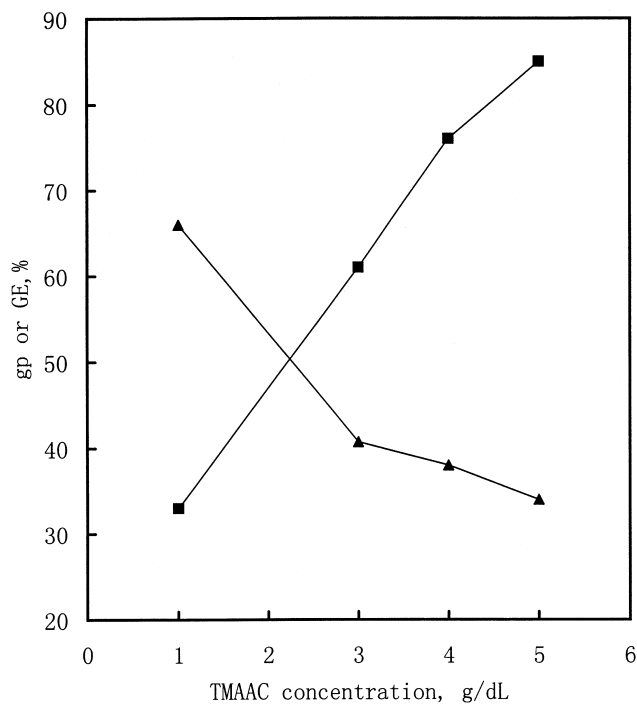


Figure 5. Effect of monomer concentration on the grafting: (■) GP; (▲) GE. Conditions: CMC, 2.0 g / dL; KMnO_4 , $0.20 \times 10^{-2} M$; H_2SO_4 , 0.25 N.

Due to environmental issues, growing efforts have been put forward in developing modified natural polymer-based hydration suppressant that may guarantee biodegradability [16-20].

By considering the nature of the functional groups present in the graft copolymers, a preliminary exploration on the possibility of grafted CMC as clay-hydration suppressant was done. To carry out the test, two water-soluble graft copolymers with different percentages of grafting were used, and the expansion of clay in their aqueous solutions along with in H_2O and in CMC solution was measured respectively using clay-hydration swelling apparatus. The results given in Figure 7 show that the grafted CMC can lower more effectively the hydration expansion of clay in water than ungrafted CMC, indicating that the grafting enhances the ability of CMC for clay-hydration suppression. Thus, it is anticipated that a new clay-hydration suppressant with good environmental acceptability may be prepared by manganese(IV)-initiated grafting TMAAC

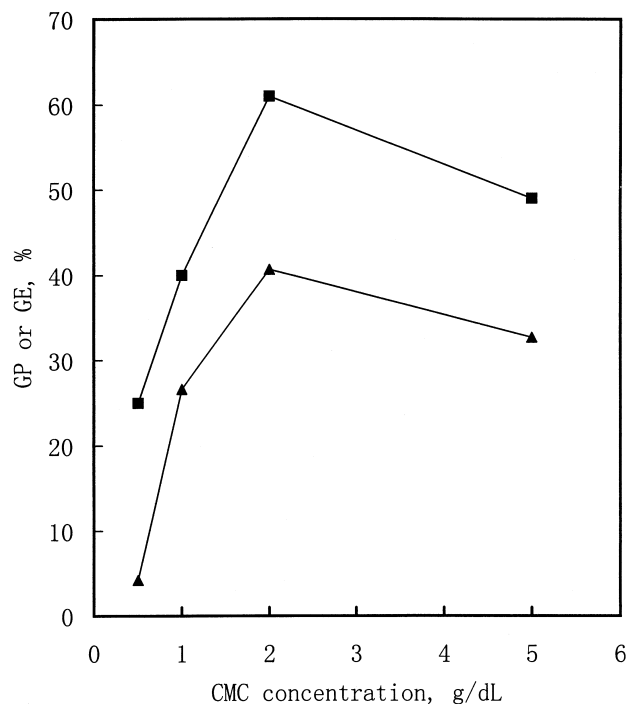


Figure 6. Effect of CMC concentration on the grafting: (■) GP; (▲) GE. Conditions: TMAAC, 3.0 g/dL; KMnO_4 , $0.20 \times 10^{-2} M$; H_2SO_4 , 0.25 N.

onto CMC. Further works on the relationship between the structure of these graft copolymers and their properties are now in progress.

CONCLUSION

Poly (TMAAC) could be grafted onto CMC in aqueous medium by using potassium permanganate/sulphuric acid system as redox initiator. It was possible to control the extent of grafting by varying the reaction conditions. The grafting reaction may be characterized by first producing free radicals on the CMC macromolecular backbone and then adding TMAAC molecules to formed CMC macro-radicals. The grafted CMC has amphoteric structure. In addition, the grafted CMC could lower more effectively the hydration expansion of clay than ungrafted CMC, showing a potential use as a new clay-hydration suppressant for oilfield.

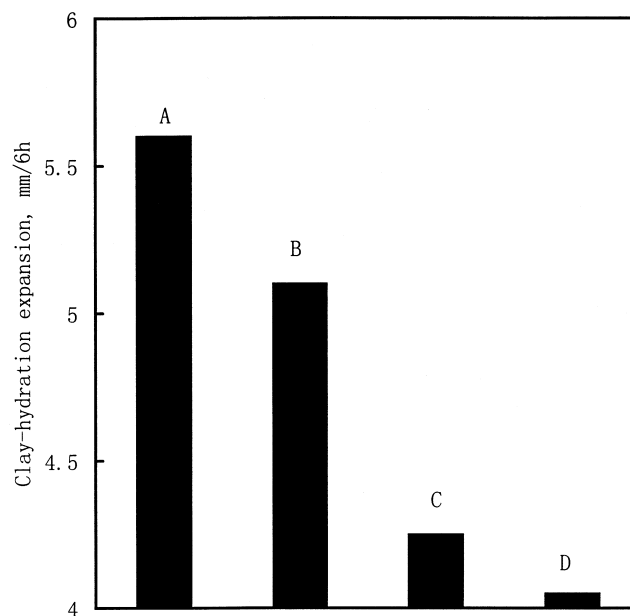


Figure 7. Hydration expansion of clay after it has contacted various fluids (A) H₂O; (B) 0.6% CMC solution; (C) 0.6% grafted CMC solution (GP=25%); (D) 0.6% grafted CMC solution (GP=33%).

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