A novel redox system, potassium diperiodatocuprate(III) (DPC) sodium alginate (SA), was employed to initiate the graft copolymerization of methyl acrylate (MA) onto SA in alkali medium. The effects of reaction variables, such as the initiator concentration, the ratio of monomer to SA, the SA backbone concentration, as well as temperature and time, were investigated, and the grafting conditions were optimized. Graft copolymers with both high grafting efficiency and high percentage of grafting were obtained, indicating that DPC SA redox system is an efficient initiator for this graft copolymerization. The structures and the thermal stability of SA and SA-g-PMA were characterized by scanning electron microscope, infrared spectroscopy and thermogravimetric analysis. A mechanism is proposed to explain the generation of radicals and the initiation.

**ABSTRACT**

A novel redox system, potassium diperiodatocuprate(III) (DPC) sodium alginate (SA), was employed to initiate the graft copolymerization of methyl acrylate (MA) onto SA in alkali medium. The effects of reaction variables, such as the initiator concentration, the ratio of monomer to SA, the SA backbone concentration, as well as temperature and time, were investigated, and the grafting conditions were optimized. Graft copolymers with both high grafting efficiency and high percentage of grafting were obtained, indicating that DPC SA redox system is an efficient initiator for this graft copolymerization. The structures and the thermal stability of SA and SA-g-PMA were characterized by scanning electron microscope, infrared spectroscopy and thermogravimetric analysis. A mechanism is proposed to explain the generation of radicals and the initiation.

**INTRODUCTION**

Algin or alginate is a gelatinous substance produced by brown algae, and is used in a wide range of food, leather, pharmaceutical, and industrial applications. Because it is one of the few hydrocolloids that are capable of both thickening and gelling water, algin offers many useful properties, such as viscosity control, stabilization of suspensions, emulsions and foams, improved freeze or thaw stability, film formation, rheology control, and more. Algin has so many useful properties...
and it is a very user and consumer friendly, as it is renewable, biodegradable, vegetable and wholly safe by all known tests [1]. But alginate is prone to enzymatic degradation and suffers from limitation in fabrication, which limits its application in some fields, for example in controlled release technology [2].

Grafting is a well-established and powerful method to develop natural and synthetic polymer hybrid materials. Among the chemical initiation methods, redox-initiated grafting offers advantages since, in the presence of redox system, grafting can be carried out under milder conditions and side reactions are at a minimum. So far, grafting of vinyl monomers onto alginate has been carried out using ceric (IV) ions [3-7], persulphate [8], redox pair of persulphate with urea [9] or thiourea [10], hydrogen peroxide [11], hydrogen peroxide coupled with ferrous [12] or ascorbic acid [13] et al. With these initiators, ceric (IV) ions were employed most extensively due to the higher extent of grafting compared to the others. But its high price and acid reactant medium limit its broad application.

Nowadays, the basic theoretical research and application on supernormal valence transitional metals have received considerable attentions. In recent years, we have also obtained some achievements on the homopolymerization and graft copolymerization of vinyl monomers initiated by supernormal valence transition metals, such as diperiodatocuprate (III) [14-16], diperiodatoargentate (III) [17-18] and diperiodatonicelate (IV) [19-22]. It has been demonstrated that DPC is an efficient and cheap initiator.

In this paper, graft copolymerization of methyl acrylate onto sodium alginate was investigated in detail, using DPC-SA redox pair as initiator and in an alkaline medium. It is superior to ceric ion due to the solubility of SA in water and the insolubility of SA in acid aqueous solution, which would further resulted in the higher grafting efficiency. At the same time, some structure and properties of graft copolymers were characterized by SEM, IR and TGA. A tentative mechanism is proposed to explain the formation of radicals and the initiation.

**EXPERIMENTAL**

**Materials**

Sodium alginate (viscosity range:1.05-1.15Pa.s), obtained from Damao Chemical Reagent station, was washed with acetone to remove any adhering impurity before use and then dried under reduced pressure. MA, from Tianjin Huadong Chemical Reagent Station, was washed successively with aqueous sodium hydroxide solution and distilled water, and then drying over anhydrous sodium sulphate and distilled under reduced pressure. DPC was synthesized and measured according to the reported procedure [23]: CuSO₄·5H₂O (5.53 g), KI₂O₄ (6.80 g), KOH (9.0 g) were added to about 250 mL of water. The mixture was shaken thoroughly and heated on a hot plate. In about 20 min the boiling mixture turned intensely red and the boiling was continued for further 20 min for the completion of the reaction. The mixture was then cooled, filtered through sintered glass crucible (G-4) and diluted to 250 mL with doubly distilled water. The concentration of DPC was obtained by its absorption at λ = 414 nm using a Shimadzu UV-265 spectrophotometer (Japan). The concentration of base DPC was calculated as 0.025 M. The other solvents were all of analytical reagent and used as such.

**Graft Copolymerization**

In a typical experiment, the graft copolymerization was carried out as follows: a required amount of sodium alginate was dissolved completely in water in a 50 mL conical flask, and the required amount of aqueous potassium hydroxide solution and aqueous acetic acid solution were added to maintain the same alkalinity in the reaction system. The flask was stoppered and deaerated sufficiently by sparging with nitrogen and were equilibrated at required temperature with constant stirring. Then the monomer was injected, followed by DPC aqueous solution, and the total volume of the reaction mixture was made up to 28 mL with distilled water. After a required reaction time, the reactant was cooled and neutralized by aqueous acetic acid solution and then it was poured into excess of methanol to precipitate the crude copolymer. The precipitated product was filtered through weighed sintered glass funnel, washed to neutral with methanol and dried to a constant weight under vacuum at 60°C. The homopolymer of methyl acrylate (PMA) was removed from the crude graft copolymer by exhaustive Soxhlet extraction with acetone for 48 h. The final copolymer was then dried to a constant weight under vacuum. The above process
was repeated for the variable temperature, time, monomer concentration, initiator concentration as well as the SA backbone concentration.

The grafting parameters, such as total conversion (C), grafting efficiency (GE) and percentage of grafting were defined and calculated as follows:

\[
C(\%) = \left( \frac{\text{total weight of PMA}}{\text{weight of MA charged}} \right) \times 100
\]

\[
GE(\%) = \left( \frac{\text{weight of PMA grafted}}{\text{total weight of PMA}} \right) \times 100
\]

Percentage of grafting (\%) = \left( \frac{\text{weight of PMA grafted}}{\text{weight of SA}} \right) \times 100

**Measurements**

**SEM**

Scanning electron microscope, AMKAY-1000B was used to observe the morphologies of SA and SA-g-PMA.

**FTIR Spectroscopy**

The FTIR spectra of the pure SA and SA-g-PMA were recorded on an FTS 40 spectrometer (Bio Rad Co. USA) using potassium bromide pellets technique.

**Thermal Analysis**

TGA curves of ungrafted and grafted SA were carried out on a Shimadzu apparatus (DGC-40 DTA-TG) at a heating rate of 10°C /min in a static air atmosphere.

**RESULTS AND DISCUSSION**

**Effect of DPC Concentration**

As it is shown in Figure 1, when the total volume, the ratio of MA/SA as well as reaction temperature, time and pH are kept constant, by varying the DPC concentrations, C and percentage of grafting increase significantly first by reaching a maximum value, and then decrease slightly. The initial increasing trend maybe due to the fact that in this concentration range, DPC attacks the characteristic group (OH) of SA backbone directly, and creates a great deal of grafting sites, which will initiate the grafting in the presence of MA. As a result, C and percentage of grafting grow sharply. However, an excess of DPC will accelerate the oxidation of radicals by DPC and the propagating chain will be terminated. Whereas, grafting efficiency keeps at a high level and almost unchanged at first and afterwards declines slightly. The decline of grafting efficiency maybe due to the enhanced chance of the transfer reaction to monomer.

**Effect of Monomer/Sodium Alginate Ratio**

The effect of monomer-to-sodium alginate ratio on graft copolymerization of MA onto SA is depicted in Figure 2. It is observed from this figure that C and percentage of grafting increase initially with the increasing MA-to-SA ratio, but beyond MA/SA = 4.59, percentage of grafting increases continuously, while C decreases. At the same time, grafting efficiency increases in the beginning and thereafter remains con-
stant. The initial increasing trend of all the grafting parameters may be ascribed to the surface activity and self-emulsifying properties of SA and SA-g-PMA, which assist in the higher availability of monomer molecules to the growing chains and active sites on the SA. The following decreasing trend of C may be due to very large ratio of MA to DPC, namely, the DPC is relative deficient to the superabundant of MA, although the absolute amount of grafted polymer increases, as evidenced by an increase in percentage of grafting all the time, whereas it decreases in relation to the fast increase of MA.

**Effect of Backbone Concentration**

Figure 3 exhibits the influence of SA concentration, as evident by total conversion C and percentage of grafting decrease steadily with the increased of SA concentration. However, grafting efficiency increases first and thereafter declines. It may be explained that an increase in backbone concentration can make more monomers and initiators easily approachable to the surface of SA and produce more grafted side chains which cause grafting efficiency to increase. The decreasing trend of all the parameters may be explained as follows: firstly, the high viscosity of the reaction system make the diffusion of both monomer and DPC to SA difficult, thus the rate of grafting will be hindered greatly. Besides, the difficulty of DPC diffusion leads to a higher local DPC concentration, which makes the rate of termination accelerate due to the reaction between the propagating chain radicals and primary radicals as well as the oxidation of the radicals by DPC. In addition, the decrease in monomer-to-backbone ratio is also account for the decrease of percentage of grafting. Similar observations have also been reported in the case of ceric-induced grafting of ethyl acrylate onto sodium alginate [3].

**Effect of Temperature**

The grafting reactions were carried out at different temperatures between 20°C and 60°C, keeping the other variables constant. As shown in Figure 4, total conversion and percentage of grafting increase in the beginning up to 30°C and decrease to some extent with further increase of temperature to 60°C. However, GE remains almost unchanged in the range studied. The improvement in total conversion and percentage of grafting may be due to the higher rate of dissociation of initiator, enhanced ionization of SA (which attracts more DPC) as well as the quickened diffusion and mobility of the monomer molecule from the aqueous phase to the backbone with the increase in temperature. The decline of total conversion and percentage of grafting with further increased temperature can be ascribed both to the enhanced radical termination reaction through oxidation by DPC and to increased chance of chain transfer reaction.

**Effect of Time**

Figure 5 illustrates the influence of reaction time on
grafting parameters. It can be seen that, after 15 min
(for the induction period before 15 min), GE stays
unchanged during the course of the reaction, whereas
both total conversion and percentage of grafting
increase steadily with the reaction time prolonged up to
35 min, and then maintain a plateau, which is in consis-
tent with the general rule of conventional radical poly-
merization. So the optimized reaction time is 35 min.

IR Spectroscopy
The proof of grafting was obtained from the FTIR
spectra of pure SA, and SA-g-PMA after exhaustive
Soxhlet extraction with acetone. As shown in Figure 6,
in the spectrum of SA, the characteristic peaks, It can
be observed the absorption bands around 1613 cm⁻¹
and 3414 cm⁻¹, are attributed to stretching vibration
bands of carboxylate and of hydroxyl groups, respec-
tively. In the spectrum of the graft copolymer, besides
retaining the above-mentioned bands of pure SA, it
shows an additional stronger absorption band at 1737
cm⁻¹, characteristic absorption of ester carbonyl groups
in PMA of the copolymer, which confirmed the forma-
tion of SA-g-PMA effectively.

Scanning Electron Microscopy
The scanning electron micrographs of pure SA and SA-
g-PMA are shown in Figure 7. It is obvious that the sur-
face of pure SA is very rough and brittle, whereas the
surface of SA-g-PMA tends to be smoother and has

Figure 5. Effect of time on grafting parameters:
c(DPC) = 0.89 x 10⁻³ mol/L, MA/SA (weight) = 4.59, SA = 0.25 g,
T = 25°C.

Figure 6. Infrared spectra of a SA and b SA-g-PMA.

Figure 7. SEM Micrographs of a SA and b SA-g-PMA.
almost turned into an entirety, which may be due to the incorporation of PMA with the SA backbone.

**Thermal Analysis**

Thermogravimetric analysis (TGA) of pure SA and the grafted copolymer is shown in Figure 8. It is evident that the TGA of pure SA shows a weight loss in three stages. The first stage ranges from 44.1°C to 188°C and shows about 6.27% weight loss. This may correspond to the loss of residual or absorbed moisture. No such inflexions are observed in the TGA curve of SA-g-PMA. This reveals that graft copolymer is resistant to moisture absorption owing to the incorporation of hydrophobic PMA chain. The second stage referred to as pyrolysis starts at 188.0°C and continues up to 516.0°C, during which there is 52.08% weight loss due to the degradation of macromolecular chain. However, the pyrolysis of the grafted copolymer can be divided into two steps, the initial step before 308.0°C, at which about 20.25% weight loss, maybe caused by the degradation of some ungrafted SA. The latter step occurs between 308.0°C and 507.9°C, with about 49.38% weight loss, which is probably attributed to the degradation of the grafted copolymer. The last stage (after 500°C) of SA and the graft copolymer have a weight loss of 16.32% and 16.86%, respectively as a result of carbonization. In addition, it is also evident from the TGA curve that the temperature at 50% weight loss of grafted copolymer is 349.8°C, higher than that of pure SA (at 316.1°C), which illustrates that the thermal stability of the grafted copolymer has improved.

**The Initiation Mechanism of Grafting Reaction**

SEM, IR spectra and TGA show that PMA has been grafted onto SA. Infrared spectra analysis can also be used to prove the grafting sites by the variation in the intensity of the -OH absorption band, in which it was found that the intensity of the -OH band in the spectrum of SA-g-PMA is weakened, which indicates that the grafted chains are linked through the hydroxyl groups. So a tentative initiation mechanism based on a single-electron-transfer process of DPC was proposed as follows:

![Figure 8. Thermal analysis for a SA and b SA-g-PMA.](image)

**CONCLUSION**

Graft copolymerization of MA onto SA in an aqueous alkaline medium initiated by DPC can be carried out successfully. The proof of grafting was obtained from IR analysis. Based on the TGA results, it was found that the grafted SA was more thermally stable than ungrafted one due to the incorporation of PMA, which may broaden the range of SA application. In addition, as it was evident from the SEM micrographs, the morphology was also changed greatly after grafting.

During this research, graft copolymers with high graft efficiency and grafting percentage have been obtained. DPC-SA System is found to be an efficient redox initiator for this graft copolymerization. At the same time, DPC was obtained from CuSO₄·5H₂O, cheaper than other initiators, which makes it favourable to facilitate its application. Furthermore, the graft reaction is attainable at a mild temperature and in alkaline aqueous medium. Thus DPC-SA redox system is considered to be a practical initiator and has a good foreground.

**REFERENCES**

2. Philipp B., Bock W., Schierbaum F., Application of poly-


