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WATER-SOLUBLE AMPHOLYTIC GRAFTED POLYSACCHARIDES. 1. GRAFTING OF THE ZWITTERIONIC MONOMER 2-(2-METHACRYLO-ETHYLDIMETHYLAMMONIO) ETHANOATE ONTO HYDROXYETHYL CELLULOSE

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WATER-SOLUBLE AMPHOLYTIC GRAFTED POLYSACCHARIDES. 1. GRAFTING OF THE ZWITTERIONIC MONOMER 2-(2-METHACRYLOETHYLDIMETHYLAMMONIO) ETHANOATE ONTO HYDROXYETHYL CELLULOSE

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Key Words: Grafted Polysaccharides, Polyampholyte, Zwitterionic Monomer, Hydroxyethyl Cellulose, Graft Copolymerization

ABSTRACT

Novel ampholytic grafted polysaccharides were prepared by grafting the zwitterionic monomer 2-(2-methacryloethyl-dimethylammonio) ethanoate onto hydroxyethyl cellulose. Ethylenediamine tetraacetic acid was used in combination with ceric ammonium nitrate as the redox initiator. The effects of various factors such as initiator amount, monomer concentration, reaction temperature and time on the grafting were studied and the optimum reaction conditions to obtain maximum degree of grafting were found. The resulted graft copolymer was characterized by IR and thermal analyses.

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INTRODUCTION

In recent years, the preparation of water-soluble polymers containing both anionically and cationically charged species has been an area of increasing interest due to the various commercial applications of these materials including water purification, frictional drag reduction, petroleum recovery, fluid modification, controlled drug release, and personal care formulations [1-21]. They have been synthesized by copolymerization of both anionic and cationic monomers into the polymer backbone [1-10], by appropriate modification of preformed polymers [11-13] or by incorporating into the polymer zwitterionic monomer units [14-21]. Of particular interest is the preparation from solfobetaine-type or carboxybetaine-type zwitterionic monomers. These zwitterionic monomers are unique in that the cationic and anionic charges are incorporated into the same mer unit and the resulting polyzwitterions can exhibit pH- or electrolyte responsiveness [14-21], which is especially important for developing "smart" rheological fluids.

While a number of investigations have focused on synthetic polyampholytes, much less attention has been paid to ampholytic grafted polysaccharides except our recent reports [22-26]. Polysaccharides belong to an important class of macromolecules not only because of their abundant source and low cost but also their biodegradability and lack of toxicity. In this work, new water-soluble ampholytic grafted polysaccharide was prepared by ceric ion-initiated grafting of the carboxybetaine-type zwitterionic monomer 2-(2-methacryloethyl dimethylammonio) ethanoate (MAEDAE) onto hydroxyethyl cellulose (HEC). The major factors affecting the graft copolymerization, such as initiator concentration, monomer amount, reaction temperature and time, were studied and the obtained graft copolymer was characterized by IR and thermal analyses.

EXPERIMENTAL

Materials

Commercial HEC obtained from Hoechst Co., Germany were used. Its molecular weight is 4.56×10^5 (H_2O , 25°C), determined by viscosity method [27]. 2-(Dimethylamino)ethyl methacrylate (DMAEM) was supplied by Jilu Petroleum Chemical Company in China and purified by distillation under reduced pressure. Sodium hydroxide, sodium monochloroacetate (MCA), ceric

ammonium nitrate (CAN), nitric acid and ethylenediamine tetraacetic acid (EDTA) were of analytical grade.

Synthesis of Zwitterionic Monomer

Zwitterionic monomer MAEDAE was prepared by the reaction of the vinyl monomer DMAEM with sodium monochloroacetate (MCA) [28]. Into a 150 mL flask equipped with a stirrer, condenser, and thermometer, DMAEM (30.0 g), MCA (22.2 g), H₂O (10 mL), and a trace of hydroquinone used as an anti-polymerization agent were added. The contents were stirred under N₂ at 80°C for 4 hours, and then allowed to stand at 5°C for two days. The precipitated white crystals were collected by filtration, washed with the ethyl ether/acetone mixture several times, and dried under reduced pressure to obtain MAEDAE (yield: 92.5%). Analysis for C₁₀H₁₇: Calcd.: C, 55.81%; H, 7.95%; N, 6.51%. Found: C, 55.67%; H, 7.58%; N, 6.50%. FTIR (KBr pellet): aliphatic C–H, 2973 cm⁻¹; ester C=O, 1721 cm⁻¹; carboxylate C=O, 1639 cm⁻¹; ester C–O, 1173 cm⁻¹; quaternary ammonium C–N, 962 cm⁻¹ and 899 cm⁻¹. ¹H NMR (D₂O with 3-(trimethylsilyl)-1-propanesulfonic acid as the reference): 1.96, 3.32, 4.00, 4.16, 4.40, 5.78, and 6.18. Peak assignments are given in Figure 1.

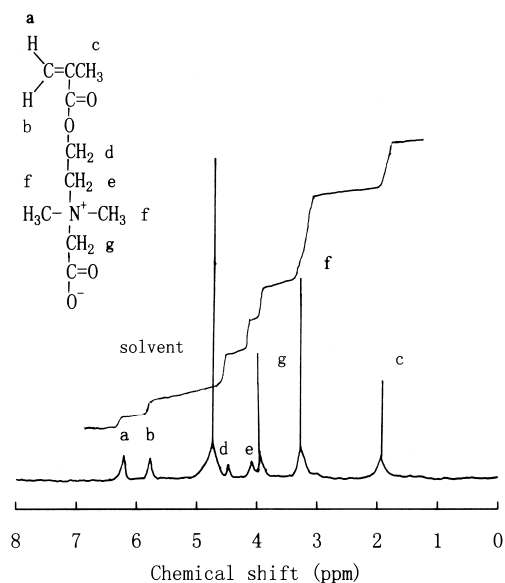


Figure 1. ¹H-NMR spectrum of the zwitterionic monomer 2-(2-methacryloxydi-methylammonio) ethanoate (MAEDAE).

Graft Copolymerization

The graft-copolymerization reaction was carried out in a 250-mL four-neck round flask equipped with a mechanical stirrer. A definite amount of HEC was dissolved with stirring and warming in distilled water, and purified nitrogen was purged. After 30 minutes, the initiator solution was added to the reaction system. After 10 minutes, the zwitterionic monomer MAEDAE was added. The flask content was kept in a thermostatic water bath at different temperature (15–60°C) for the required time. The reaction product was precipitated by pouring the reaction mixture solution into acetone, filtered and washed with acetone for several times, then dried under reduced pressure to constant weight. To obtain the pure graft copolymers, the reaction product was slurried in aqueous methyl alcohol followed by filtration and finally dried in vacuum oven at 40°C. It was found that extracting with a mixture of methyl alcohol and water was quite enough to remove the poly (DMAEM) (homopolymer). The obtained graft copolymers are water-soluble. The grafting parameters were determined as follows:

$$\text{Grafting percentage (\%G)} = (W_p - W_0) \times 100/W_0$$

$$\text{Monomer grafting conversion (\%C)} = (W_p - W_0) \times 100/W_m$$

where W_0 , W_p and W_m are the weights of HEC, purified graft copolymer and the zwitterionic monomer MAEDAE, respectively.

IR and Thermal Analyses

The IR spectra of ungrafted HEC and the graft copolymer were run on NICOLET FT-20SX spectrophotometer using KBr pellets in the range of 400–4000 cm^{-1} . Thermal analysis was measured by Perkin-Elmer Thermal Analyzer (Model TGS-50). The heating rate was at 20°C/min. in air atmosphere.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on Grafting Extent

Due to its ease of application and minimized homopolymer formation, ceric ion redox systems have gained considerable importance in the grafting reaction of cellulose or chemically modified cellulose. This technique is based on the fact that when cellulose or chemically modified cellulose is oxidized by a

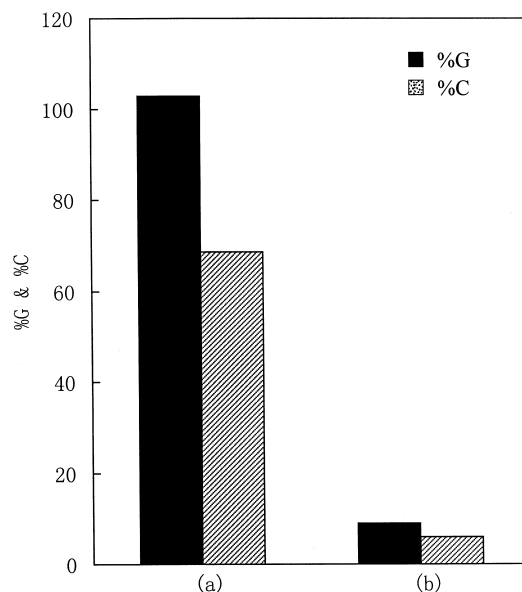
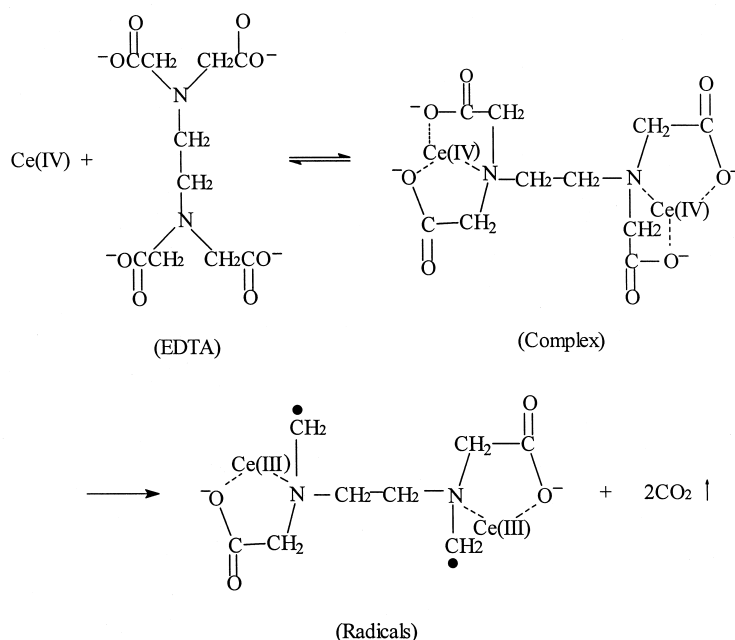


Figure 2. Comparison of initiating ability between CAN/EDTA and CAN/HNO₃ pairs: (a) initiated by CAN/EDTA; (b) initiated by CAN/HNO₃. Conditions: HEC, 2.0 g/dL; MAEDAE, 3.0 g/dL; CAN, 5.0×10^{-3} mol/L; EDTA, 5.0×10^{-3} mol/L; HNO₃, 5.0×10^{-3} mol/L; 35°C; 6 hours.

ceric ion salt such as CAN, free radicals capable of initiating vinyl polymerization are formed on the cellulose or chemically modified cellulose by a single electron transfer [29]. Acid such as nitric acid is usually used as the reducing agent in the redox systems [30-32]. Recently, Hsu *et al.* [33] indicated that amino acid-type chelating agent such as EDTA, as reducing agent for the ceric ion redox initiator, is more effective when applied in the aqueous polymerization of acrylamide.

To explore the feasible ceric ion redox initiator for the grafting of zwitterionic monomer MAEDAE onto HEC, the comparative study between CAN-EDTA and CAN-HNO₃ pairs was carried out (Figure 2). It is found that CAN-EDTA initiated graft copolymerization has much higher %G and %C than CAN-HNO₃ initiated graft copolymerization under same reaction conditions, suggesting the effectiveness of CAN-EDTA redox system as the initiator. Different from the CAN-HNO₃ redox system, the radical formation derived from the CAN-EDTA redox pair seems likely to occur through the complex formation and decomposition:



Figures 3 and 4 show the effects of CAN and EDTA concentrations on the grafting content. The concentration range studied is from 1.25×10^{-3} to 7.25×10^{-3} mol/L. It is seen that increasing CAN concentration or EDTA concentration up to 5.00×10^{-3} mol/L is accompanied by the increase in %G and %C, but beyond that point the %G and %C decrease. Interestingly, the %G and %C attain maxima when the concentrations of CAN and EDTA are 5.00×10^{-3} mol/L. Obviously, the grafting extent would be enhanced if the free radicals formed on the HEC macromolecule are capable of capturing the monomer and would be reduced if the active sites on the HEC macromolecule are combined with other agents rather than the monomer. Also, formation of homopolymer will compete with grafting. From our experiment, the extensive homopolymerization of MAEDAE was observed at high initiator concentration ($>5.00 \times 10^{-3}$ mol/L).

The effect of MAEDAE concentration on the grafting content is illustrated in Figure 5. The %G increased remarkably with increasing MAEDAE concentration from 1.0 to 4.0 g/dL, whereas the %C increased with increasing MAEDAE concentration from 1.0 to 3.0 g/dL and then decreased slightly with further increasing MAEDAE concentration. The increment in the %G and %C could be interpreted in terms of the greater availability of monomer molecules in the proximity of the HEC at higher MAEDAE concentration. It is understand-

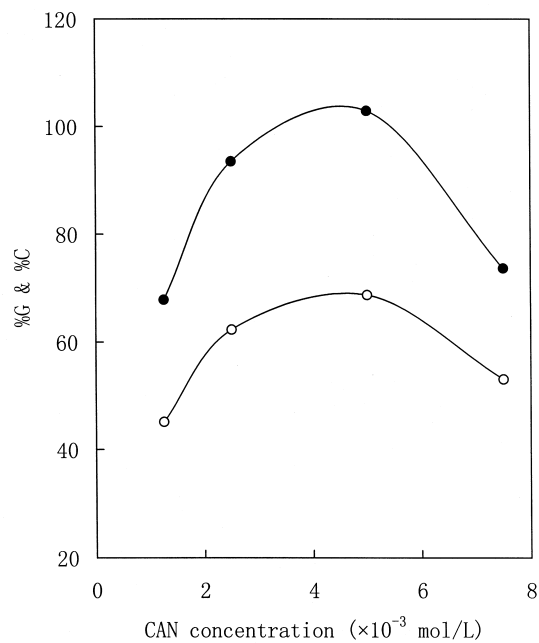


Figure 3. Effect of CAN concentration on the grafting content: (●) %G; (○) %C. Conditions: HEC, 2.0 g/dL; MAEDAE, 3.0 g/dL; EDTA, 5.0×10^{-3} mol/L; 35°C; 6 hours.

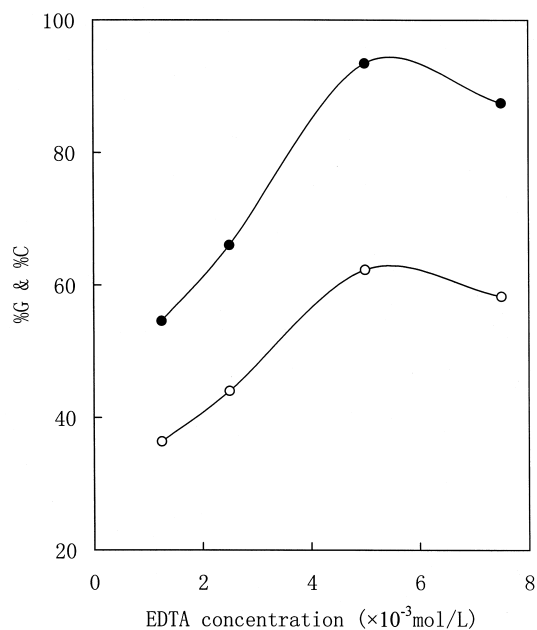


Figure 4. Effect of EDTA concentration on the grafting content: (●) %G; (○) %C. Conditions: HEC, 2.0 g/dL; MAEDAE, 3.0 g/dL; CAN, 2.5×10^{-3} mol/L; 35°C; 6 hours.

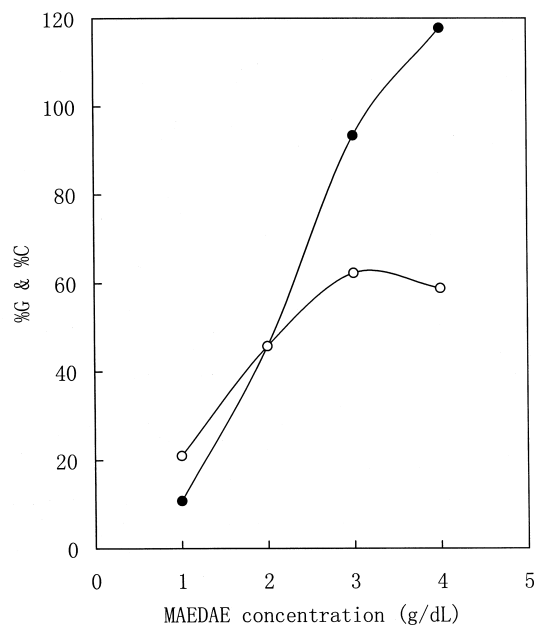


Figure 5. Effect of MAEDAE concentration on the grafting content: (●) %G; (○) %C. Conditions: HEC, 2.0g/dL; CAN, 5.0×10^{-3} mol/L; EDTA, 5.0×10^{-3} mol/L; 35°C; 6 hours.

able that the active centers on the HEC molecules are relatively immobile. Reaction of these macro-radicals with the monomer would, therefore, essentially depend on the availability of the monomer in their vicinity [34]. The slight decrease in the %C at the concentration of 4.0 g/dL may be attributed to the increase of homopolymer.

The graft polymerization was carried out at different temperatures ranging from 15-60°C. The relation between the grafting extent and the polymerization temperature is illustrated in Figure 6. It is noted that higher %G and %C could be obtained even at low temperature of 15°C. The maximum graft extent was observed at 35°C. Compared with the graft polymerization initiated by CAN-HNO₃ redox system [30-32], CAN-EDTA initiated graft copolymerization in this study seems to occur and proceed more easily. This may be ascribed to that the latter needs lower reaction activation energy. Beyond 35°C, the %G and %C decreased. This is probably because that the termination rate of grafted chain-free radicals and the rate of homopolymerization increased with further increasing the temperature.

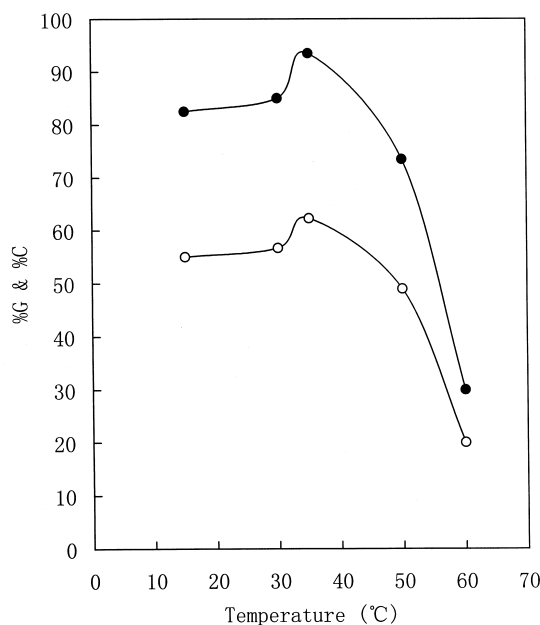


Figure 6. Effect of temperature on the grafting content: (●) %G; (○) %C. Conditions: HEC, 2.0g/dL; MAEDAE, 3.0 g/dL; CAN, 5.0×10^{-3} mol/L; EDTA, 5.0×10^{-3} mol/L; HNO_3 , 5.0×10^{-3} mol/L; 6 hours.

Figure 7 shows that the effect of reaction time on the grafting of MAEDAE onto HEC. It is clear that the grafting is characterized by an initial fast rate following by a slower rate which levels off after a certain time. Leveling off of grafting with time could be attributed to a decrease in concentration for both initiator and monomer as well as to a reduction in the number of sites on the HEC backbone accessible for grafting as the reaction proceeds.

Characterization by IR and Thermal Analyses

The IR spectra of ungrafted HEC and the graft copolymer (%G = 54.6) are given in Figure 8. For ungrafted HEC, it showed a broad absorption band in the region of $4000\text{--}3000\text{ cm}^{-1}$, in addition to bands occurring at 2920 cm^{-1} and 1125 cm^{-1} , which belong to C-H stretching vibration in methylene groups and C-O-C antisymmetric stretching vibrations, respectively. In contrast, the IR spectrum of the graft copolymer showed not only the characteristic absorption bands

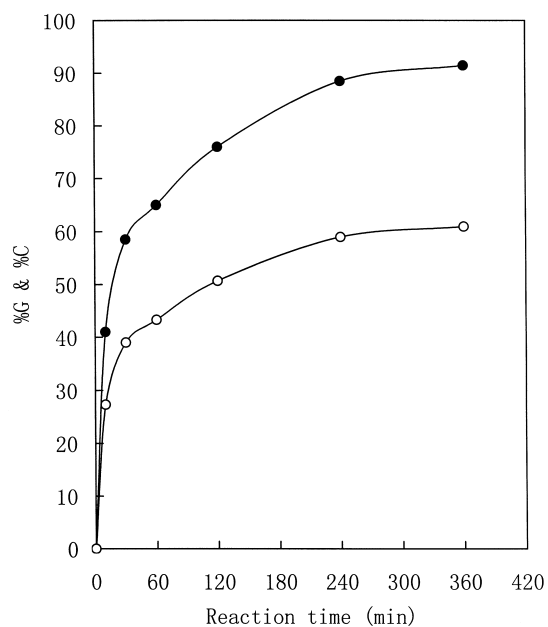


Figure 7. Effect of reaction time on the grafting content: (●) %G; (○) %C. Conditions: HEC, 2.0g/dL; MAEDAE, 3.0 g/dL; CAN, 5.0×10^{-3} mol/L; EDTA, 5.0×10^{-3} mol/L; HNO_3 , 5.0×10^{-3} mol/L; 35°C.

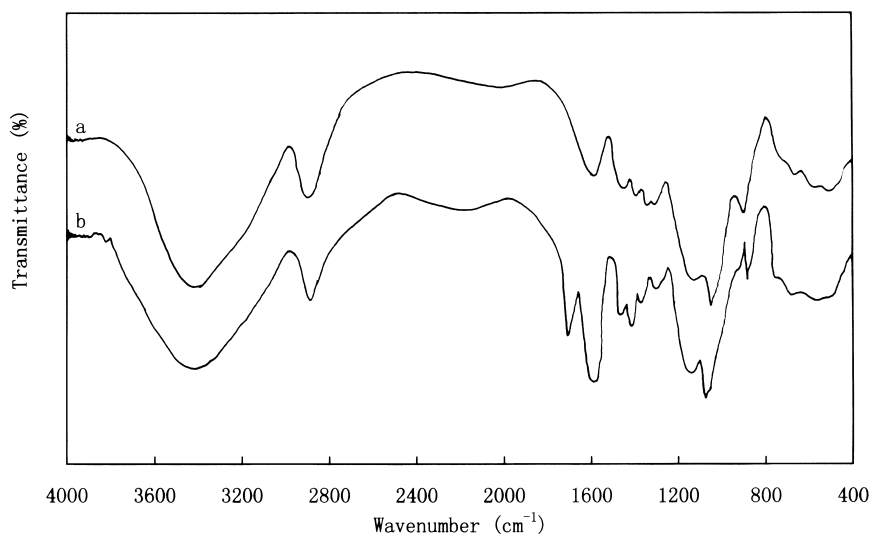


Figure 8. IR spectra of (a) HEC and (b) the graft copolymer (%G = 54.6).

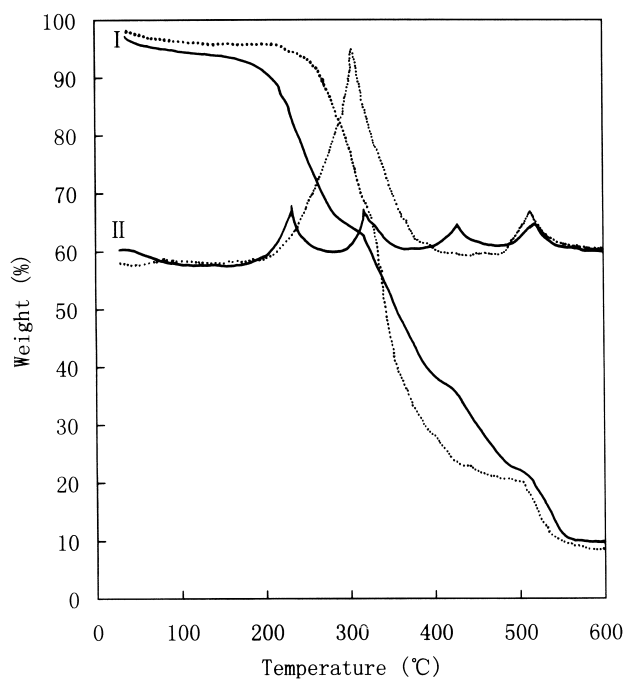


Figure 9. The curves of (I) TG analysis and (II) derivative TG analysis obtained under an air atmosphere degradation of HEC (-----) and the graft copolymer (—).

of HEC but also additional band at 1728 cm^{-1} , which is characteristic of ester $\text{C}=\text{O}$. Besides, the differences in the bandwidths and intensities of some absorption bands were observed. These indicate that the graft copolymer contains the chain structure of MAEDAE unit.

Figure 9 gives the thermogravimetric (TG) and derivative TG curves for the thermal degradation of HEC and the graft copolymer ($\%G = 54.6$), with a heating rate of $20^\circ\text{C}/\text{min}$. under an air atmosphere. For ungrafted HEC, the thermal degradation occurs in two distinct stages and two maximum peaks appear at 301.8°C and 505.0°C , characteristic of the degradation of cellulose chain and hydroxyethyl substituents, respectively. For the graft copolymer, however, the derivative TG curve shows four maximum peaks at 233.5 , 309.0 , 428.0 , and 508.0°C . The peaks at 309.0°C and 508.0°C result from the thermal degradation of the substrate HEC. The peaks at 233.5°C and 428.0°C are attributed to the thermal degradation of MAEDAE graft chain.

CONCLUSION

The new graft copolymer of hydroxyethyl cellulose with the carboxybetaine-type zwitterionic monomer 2-(2-methacryloethyltrimethylammonio) ethanoate (MAEDAE) was prepared by using CAN-EDTA as the redox initiator and was characterized by IR and thermal analyses. The major factors affecting the graft copolymerization were investigated. The optimum reaction conditions to obtain maximum degree of grafting were found as follows: the concentrations of CAN and EDTA are both 5.0×10^{-3} mol/L, the reaction temperature is 35°C and the grafting time is 6 hours. Further studies will focus on the aqueous solution behavior of this novel ampholytic grafted polysaccharide and its application.

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